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PRELIMINARY REPORTS, MEMORANDA AND TECHNICAL NOTES
OF THE MATERIALS RESEARCH COUNCIL SUMMER CONFERENCE
HELD AT LA JOLLA, CALIFORNIA, JULY 1973
VOLUME II. PROCEEDINGS OF THE DISCUSSION GROUP ON
SOLAR ENERGY CONVERSION

MICHIGAN UNIVERSITY

PREPARED FOR
ADVANCED RESEARCH PROJECTS AGENCY

JULY 1973
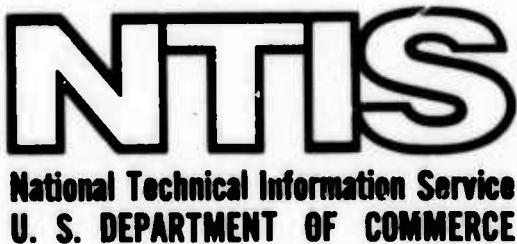
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VOLUME II

PROCEEDINGS

of the

DISCUSSION GROUP ON SOLAR ENERGY CONVERSION

i

VOLUME II   TABLE OF CONTENTS

DISCUSSION GROUP ON SOLAR ENERGY CONVERSION

R. Kaplow, A. L. Bement and M. Cohen

I.   Introduction

A three-day group discussion on solar energy conversion was held at La Jolla, California, on July 5, 6 and 7, 1973. The attendees are listed in Table I, at the end of this section of the proceedings. The program is given below:

Thursday, July 5, 1973

> Arden Bement: Overview of Some Proposed Solar Energy Conversion Schemes
>
> Roy Kaplow: Review of Some Ongoing and Proposed Materials Work Relating to Solar Energy
>
> Stanley Ruby: ARPA's Interest in Solar Energy
>
> Richard Bleiden: NSF's Energy Program in Solar Energy
>
> Joseph Loferski: The Physics and Technology of Solid State Direct Conversion Devices
>
> John Light: Photochemical Conversion Processes and Technology

Friday, July 6, 1973

> Clarence Zener: Power from Sea Thermal Gradients; Engineering Optimization
>
> Michael Bever: Applications of Solar Energy

Agenda Discussions:

Photovoltaic Cells: Joseph Loferski, Discussion Leader

Solar Thermal Collection: Roy Kaplow, Discussion Leader

Hydrogen Transmission: John Howe, Discussion Leader

Saturday, July 7, 1973

Workshop Sessions in Photovoltaics, Light Concentration and Collection, Hydrogen Transport, Hydrogen Production and Fuel Cells, Photochemical Conversion, and Sea Thermal Gradients.

The impetus for organizing the above program grew out of a two-day workshop on materials for energy conversion held at Centerville, Massachusetts, on July 20-21, 1972. This workshop examined materials problems associated with several selected energy conversion technologies to include solar, fast breeder reactors, light-water and gas-cooled fission reactors, fusion reactors, magnetohydrodynamics, and steam and gas turbines. From this workshop it was concluded that in-depth materials studies in support of advanced energy conversion, transmission, and utilization technologies are needed in order to facilitate a more meaningful assessment of technical and economic feasibility and to provide adequate lead time to anticipate and solve potentially limiting materials problems. Also, from the stimulating discussions and exchanges of ideas, it became clearly evident that the ARPA Materials Research Council could make substantial contributions toward identifying and outlining solutions to many

-2-

of the materials problems associated with energy conversion
technology.

From the various conversion technologies reviewed in 1972,
solar energy conversion was selected for specific review and
study at the 1973 meeting of the Council because of its potential
value to mankind as an inexhaustable energy supply as fossil
fuels become depleted, the challenging materials problems inherent
in both direct and indirect solar energy conversion technologies,
and the rather primitive state of photovoltaic materials research
and development. Although the significant near-term impacts that
solar energy could have on thermal space conditioning and on the
prodution of renewable clean fuels by bioconversion were recognized,
the interests of the Council were primarily addressed to technol-
ogies involved in large-scale commercial generation of electric
power and the related problems in energy storage and transmission.
The topics selected for presentation and discussion during the
first two days and the subsequen. agenda discussions and workshop
sessions were arranged to serve this interest.

Two of the early presentations provided a view of ARPA
and NSF perspectives on solar energy conversion in relationship
to their existing programs. ARPA's interest in solar energy con-
version was outlined by Stanley Ruby. In 1972 approval for an
energy program within ARPA was given on the basis of previous
studies into energy usage by the Department of Defense. One of
the objectives of this program is to develop a total energy con-
cept for a military base taking into account energy needs for

industry operations and building thermal conditioning, waste heat management, and fuel requirements for transportation systems. The interest in solar energy relates to the availability of large amounts of real estate associated with military bases that could be used for solar energy collection and conversion. Also, since hydrogen production is closely associated with solar energy storage schemes, the advantages and disadvantages of hydrogen as a fuel for transportation systems relative to synthetic fuels needs to be assessed. Work to be sponsored in FY74 will consist primarily of technical assessments and analytical studies.

Richard Bleiden described initiatives and programs being sponsored by the National Science Foundation in response to their mission of coordinating the national program in solar energy utilization for terrestrial applications. In addition to a solar energy program office established within NSF-RANN for technical program administration a Solar Energy Task Force has been established within the NSF Directorate within which each of the main technology areas are represented and activities related to material research and the collection of isolation data use coordinated. Funding estimates for FY74 reflect a three-fold increase over FY73 ($12.2 M compared with $4.2 M, respectively) and are allocated as follows: $3.0 M for heating and cooling of buildings, $3.3 M for thermal conversion, $1.4 M for photovoltaic conversion, $2.7 M for renewable fuels, $1.2 M for ocean thermal gradients and wind conversion; and $0.6 M for program support.

During the course of the group discussions, a number of critical questions concerning the principal solar energy conversion technologies and their associated materials problems became evident. These questions were posed to the participants of the workshop session conducted on the third day not for the purpose of limiting the scope of discussion but rather to focus attention on apparently important issued.

1. General Questions

    a. What are the overall chances of success of the various solar energy conversion technologies?

    b. What are the primary materials problems associated with the demonstration of technical and economic feasibility?

    c. What secondary materials problems are likely to yield annoyance or economic penalties on a continuing basis subsequent to commercial adoption of the technology?

    d. What inventions relative to both system and materials design are suggested as potential solutions to the above problem?

    e. What are the time and cost estimates for solving these problems?

2. Photovoltaic Materials

    a. What materials characterization methods are required for photovoltaic cells during research and development, production, and service?

b. What are the minimum cell efficiencies required for practical terrestial energy generation?

c. What fabrication techniques will lead to lower costs?

d. How do you establish and measure stability factors and reliability?

3. Light Concentration and Collection

a. Is a high α/ε ratio needed for practical energy generation systems? If so, can selective surfaces be maintained?

b. Are vacuum pipes needed for the collection system? If so, can structural integrity be achieved within allowable costs?

c. What durability can one expect for mirrors and outer windows?

4. Hydrogen Transport

a. What new engineering test data are required concerning the effects of hydrogen in ferritic materials.

b. What specifications and standards should be instituted for the manufacture, testing, and use of pipe for hydrogen transport?

c. What materials should be selected for compressors, valves, gaskets, etc.

5. Hydrogen Production and Fuel Cells

a. What is the practicality of reversible fuel cells for energy storage?

b. What developments in electrode materials will facilitate the separation of hydrogen from water?

c. What is the corrosiveness of intermediate products in multistep processes?

d. Can new electrode materials be developed with satisfactory conductivity, gas permeability, and catalytic response to substitute for platinum and other noble metals?

Many of the above questions and others were addressed during the working sessions. In addition, members of the Council continued to work on specific aspects of solar-related systems during the ensuing period.

Shortly before the end of the Council meeting (i.e., July 25-26, 1973) a "Summary of Salient Points" was drawn up, based on the presentations and discussions, and on subsequent studies that took place during the MRC meeting. This summary is reproduced in its entirety as Section II of these Proceedings.

Section III of these proceedings is comprised of a collection of separate papers developed by participants in the solar energy activity. These include extensive analyses as well as short notes and comments and reviews as well as original concepts. The topics discussed include applications of solar energy, concentration and collection of solar energy, photovoltaic conversion, ocean thermal gradients, energy storage, and fuel cells. A brief summary of the contents of these papers is included at the beginning of Section III.

Following the Materials Research Council Meeting itself, the opportunity arose to prepare a proposal on ARPA's behalf, for a development program on the use of solar energy. Drs. Bement, Cohen, and Kaplow drafted an appropriate proposal, drawing in a significant way on the MRC discussions. The proposal calls for the development of an integrated solar energy system for a military base. In addition to major design and engineering components, the program is to include extensive materials-related projects. The draft of the full program proposal is included in these Proceedings as Section IV.

II.   Summary of Salient Points

The following items are highlights or presentations, discussions, and studies that took place during the MRC meeting in La Jolla. For the most part, these points deal only with the materials problems in various solar-related systems.

1. General

    1.1 Solar energy can contribute a significant part of the energy requirements of the United States on a reasonable time scale, both as a basic and a marginal source.

    1.2 Relatively simple low-temperature applications, such as water heating, space conditioning, and treatment of brackish water and sewerage, are now technologically feasible, and hold promise of becoming economically feasible in the near term depending on the locality. These applications are also of military as well as en-

vironmental interest, and could furnish an increasing
portion of the energy consumed in the nation.

1.3   Special attention must be directed to energy-storage
systems, which are a common requirement for virtually
all means of solar energy conversion. The development
of improved thermal-insulation materials for both high
and low temperatures would also be beneficial.

2. Concentration and Collection of Sunlight for Thermal Systems

2.1   A three-pronged search for surfaces with special optical
properties for radiative insulation should be pursued.
Each of the three aspects may be realized in the near
future; indeed, adequate materials may already exist.

2.1.1   A surface material that is stable for long periods
($\sim$20 years) at high temperatures ($\sim$500°C) is
needed for high light-concentration systems; for
this purpose, a sunlight-absorption/infrared
emission ratio (α/ϵ) as low as 2 may be acceptable.

2.1.2   A heat-mirror surface with high transparency for
sunlight and high reflectivity for infrared will
prove useful for supplementing or replacing low ϵ
coatings in the absorbing surface, and will also
find application in general insulation against
infrared radiation (windows, light bulbs, search-
lights, etc.).

-9-

2.1.3 A surface material with very high α/ϵ for use in low-temperature systems ($\sim$250°C) without light concentration should be sought; the low operating temperature will lessen the problem of thermal degradation. A new concept based on the use of small metal particles ($\sim$100Å) should be explored.

2.2 Calculations have been made which illustrate the relationship between the geometry, the light-concentration factor and the optical properties of materials used for solar thermal energy collectors. A wedge-shaped mirror geometry has been suggested for high-concentration systems.

3. Photovoltaic Cells

3.1 New emphasis should be placed on terrestrial operations without the special requirements of outerspace applications, the latter having hitherto dominated the field. Emphasis should be placed on low cost and durability; standards of reliability can be lowered, and lower efficiencies ($\sim$5-10%) should be regarded as acceptable.

3.2 The physics and metallurgy of heterojunctions need to be better understood, especially the degradation processes in otherwise economical materials, such as Cu-Cd-S.

3.3 Improved techniques for characterizing surfaces and interfaces during the fabrication of cells are necessary.

3.4 The role of grain boundaries in photovoltaic cells requires elucidation, inasmuch as polycrystalline

materials are much less expensive than the currently
used single crystals.

3.5 The possibility of developing low-cost fabrication
techniques for stacked photocells, with graded energy
gaps which will effectively utilize a greater portion
of the sunlight wavelength distribution, should be
examined.

3.6 Materials for photovoltaics should be considered in
terms of their own requirements since these may be
different than for semiconductors used in other elec-
tronic devices.

4. Photochemical and Photogalvanic Conversion

4.1 Although endo-energetic photochemical reactions and
direct photogalvanic conversion to electricity do not
look promising now for storing or utilizing solar energy,
more research on these processes may be warranted because
of their potential low cost.

5. Hydrogen Storage and Transport

5.1 Hydrogen embrittlement in gaseous H_2 requires careful
consideration and further experimental work to guard
against this potential hazard since current knowledge
is inadequate and extrapolations from seemingly relevant
experience may be misleading.

5.2 Materials problems for the handling of liquid hydrogen
are those of cryogenic technology; they have largely

-11-

been solved for small installations but probably not for large ones.

6. Hydrogen Fuel Cells

   6.1 High-temperature fuel cells involving the use of oxide ion-conducting solid electrolytes present an attractive method for the conversion of hydrogen to electrical energy. The capital cost and overall efficiency of this type of electrochemical conversion appear to be potentially competitive with other methods. Because of operation at elevated temperatures, there are no catalytic problems in such cells.

7. Ocean Thermal Gradients*

   7.1 Low-cost methods of fabricating the required high heat-transfer boiling and condensation exchanger surfaces will be one of the necessary steps in demonstrating economic feasibility for this type of energy system.

   7.2 It will be necessary to develop methods for preventing biological fouling on exchangers.

   7.3 The rate of heat transfer on the sea-water side of the heat exchangers has to be increased; ideas for doing this include roughening surfaces, production of small ridges on surfaces, and discharging hydrogen gas cathodically (the latter may be coupled with Cl discharge to control biological growth).

   _____

   *This subject was presented by Clarence Zener, but was not studied critically by the Council members.

-12-

7.4 There is an important need for efficient and low-cost
hydrolysis cells in case hydrogen and oxygen turn out
to be the most economic way of transporting the energy
produced from ocean thermal gradients.

III. Reports

In the first paper, "An Overview of Some Proposed Solar
Energy Conversion Schemes," Arden Bement summarizes many of the
most important conclusions in recent studies of potential solar
energy utilization. He describes the complete range of seemingly
possible solar-related technologies, and discusses relevant eco-
nomic and technical factors for each.

Michael Bever, in the second paper, provides an extensive
review of the already important utilization of solar energy (on
a world/historical scale) and also considers the future potential.
He examines the less-commonly thought of uses (e.g., food drying)
as well as the ones normally considered, and provides an inter-
esting categorization of applications using working-temperature
as a parameter.

In the next note in the collection, J. J. Gilman comments
on the relative emphases being given to different aspects of the
search for practical solar energy utilization. He expresses the
opinion that systems analyses are often incomplete and use un-
realistic potential cost reduction estimates, and that too little
attention is being given to sophisticated storage systems, and to
photochemical conversion techniques.

-13-

In the fourth paper, "Thermal Insulation of Window Glass,"
A. J. Sievers addresses one aspect of energy converions. He
points out through straightforward calculations that radiative
heat loss through large glass windows can be reduced with appro-
priate coatings.

The next four papers deal with some geometrical and
materials optical-property considerations relating to the collec-
tion of sunlight. J. P. Hirth's short note, "An Alternative to
Flat Area Solar Energy Absorption Unit Deployment," describes ad-
vantages in constructing tall towers of solar collectors which
can have a large effective collection area per unit area of ground
covered. P. L. Richard's article, "Optical Analysis of Thermal
Solar Energy Collection," presents an analysis of the interplay
between the design parameters of a solar collecting system, such
as the concentration factor and the operating temperature, and
the materials optical properties, such as the emissivity and re-
flectivity. He shows that a wedge-shaped collector may be an
economical design for achieving a high concentration factor. In
the next paper, A. J. Sievers gives a theoretical derivation of
the ratio between the sunlight absortivity and thermal emissivity
(α/ϵ) for a surface coated with tiny metallic particles; he points
out that such surfaces can yield desirable optical ratios for
solar thermal collectors. In "Concentration, Collection and
Insulation," Roy Kaplow (working with Sievers and Richards) pro-
vides a general discussion of a number of factors, including
focussing, radiative and other thermal losses, and surface coatings

-14-

to obtain preferred optical properties. In the light of those general considerations, recommendations are made for a program to develop specific combinations of materials surface-properties which are thought to be both valuable and achievable in the short run.

The next two papers deal with photovoltaic cells. In the first of these, Joseph Loferski provides a brief but inclusive review of the electronic theory of the photovoltaic effect and its theoretical efficiency. He points out gaps in understanding as well, he notes the lack of major materials production efforts specifically for photovoltaic cells, and he makes a number of recommendations for future work. Henry Ehrenreich, in the following note, has compiled a large number of detailed points relating to photovoltaic cells that were made during the discussions. Many of these provide specific guidelines for research.

John Light in "Photochemical Processes and Solar Energy Utilization," presents an "outline of the possibilities, practicalities and prospects of non-biological photochemical conversion on a large scale." He concludes that basic research in that direction may well be warranted, particularly with respect to the underlying processes and mechanisms in photogalvanic cells. Robert Gomer has now made an analysis of photogalvanic cells, perhaps the first one yet attempted. His analysis, applied to the iron-thionine system, appears in the next paper, and indicates that "the problems facing the practical exploitation of solar energy through photogalvanic cells are many and formidable." A

recent Russian patent covering a photogalvanic cell employing a photoreducible dye, reduction agent and a photo-catalyst was translated by Richard Gomer. However, insufficient detail was given to allow an assessment of the merit of this device.

In the paper entitled "Solar Sea Power," Clarence Zener considers some of the engineering aspects of deriving useful energy from the small sea water thermal gradient (approximately $10°C$ in the first 100 feet of depth). Noting that the operational efficiency of the boiler and condenser is a central issue, he presents detailed considerations for their design, particularly stressing means for maximizing heat transfer with low temperature differences. John Hirth has also contributed a note on the latter issue, suggesting two methods which might increase heat transfer on the seawater side of the boiler. One of these would be the installation of turbulence producing ridges, and the other the cathodic discharge of hydrogen along the exchanger. Richard Bleiden and Zener, in a separate note, raise some materials-related problems they believe may be encountered in using the thermal sea gradients. These include, for example, developing low-cost fabrication techniques for the heat exchangers and pipes, preventing biological fouling, and resisting corrosion in the heat engine turbine.

On the subject of energy storage, J. J. Gilman has written a quantitative review of flywheel devices, giving the relationships between energy capacity, flywheel shape and construction, and the mechanical properties of the flywheel material. A detailed

-16-

list of the advantages and disadvantages of flywheel storage is given two of the most striking advantages are high storage density (1000 watt hours/pound, ideally) and very high peak-power output. John Margrave, in "Chemical Systems for Storage of Solar Energy," considers another unusual approach to the energy storage problem. As an example, he describes a simple process in which thermal energy is stored through removing water by evaporation from an H_2O/H_2SO_4 mixture, and recovered through the reverse, exothermic H_2SO_4 dilution process.

R. A. Huggins and R. L. Coble, authors of the paper "Materials Problems Relating to High-Temperature Oxide Ion-Conducting Fuel Cells for the Electrochemical Combustion of Hydrogen," have considered another aspect of the energy storage problem, namely efficient means for converting hydrogen gas to electrical power. Consideration is given to the thermodynamics, engineering design, materials requirements and fabrication costs for such cells; the final appraisal is an optimistic one, but highly dependent on ceramics fabrication costs.

In the following contribution, Willis Flygare and Robert Huggins discuss a thermoelectric generator for the direct conversion of thermal to electrical energy, which is based on the use of liquid sodium as the working medium and a solid β-alumina electrolyte. The device, which has been the subject of recent patents, is shown to have both potentially high theoretical efficiency and useful power density per unit area of electrolyte.

-17-

AN OVERVIEW OF SOME PROPOSED

SOLAR ENERGY CONVERSION SCHEMES

A. L. Bement

I.   Introduction

The sun is the most powerful source of energy available
to man. The solar constant, or the energy falling in unit time
on a surface normal to a beam from the sun and external to the
earth's atmosphere at the time-mean distance from earth to sun,
is 1.36 kw/m^2 [1], which corresponds to a terrestrial insola-
tion of four quadrillion kilowatt hours of energy each day or
about one-half million times the U.S. electrical generating
capacity [2]. However, these numbers are highly misleading,
since only a small fraction of this energy can be collected
and converted to electricity. Assuming that solar energy is
convertible to process heat at 30% and to electrical energy
at 5%, it can be shown that only 150 times the present U.S.
energy needs are received as solar energy within the contiguous
48-state land area [1]. Nevertheless, this still represents
an enormous inexhaustible source of clean energy which must be
harnessed as fossil fuels become depleted.

There are a variety of energy-conversion techniques under
research consideration, and these can be classified under
direct solar radiation and solar-derived energy as illustrated
in Figure 1 [3]. Solar radiation may be converted to elec-
tricity by solar cells or may be utilized in conventional heat

FIGURE 1
(Ref. 3)

ELECTRICITY FROM THE SUN
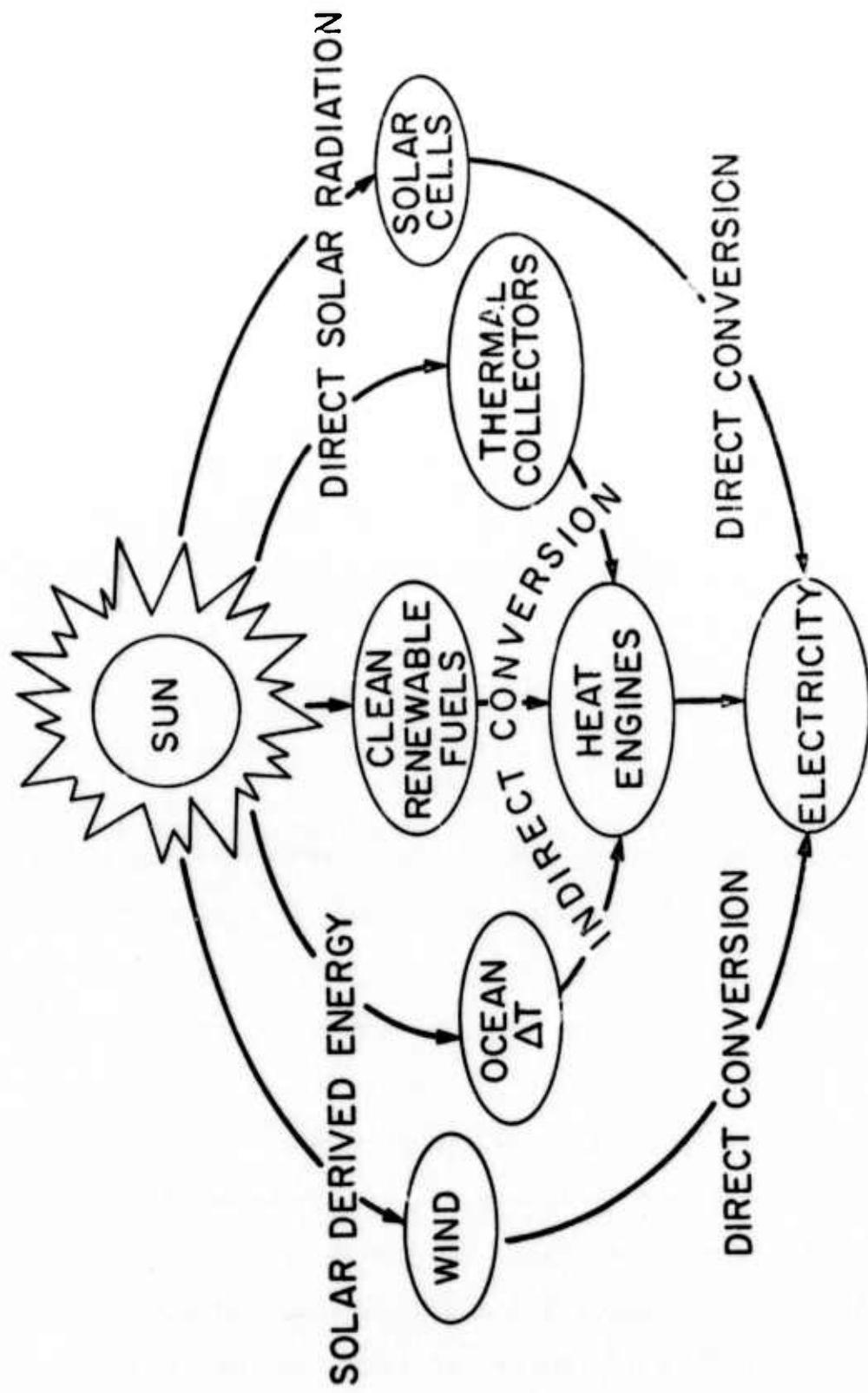
engines (such as steam turbines). Similarly solar-generated
energy in the form of winds or ocean thermal gradients can
be converted to electrical energy by means of a directly coupled
generator and a low-temperature-difference heat engine,
respectively. Fuel can also be produced by direct solar radia-
tion or from solar-derived energy. Gaseous, liquid, and solid
fuels can be produced by a variety of solar-derived processes.
Among these are photodecomposition of water; photosynthetic
growth of organic matter which can be converted to fuels by
destructive distillation, fermentation, or by high pressure
chemical processing; and photochemical conversion processes.

In January 1972, a Solar Energy Panel was organized
jointly by the NSF and NASA and was charged with assessing
both the potential of solar energy as a national energy resource
and the status of technology in the various areas of solar
energy application. Also, the panel was to recommend necessary
research and development programs to develop the potential in
those areas considered important. The report of the panel has
been recently made available [4], and some of the principal
conclusions are given below:

   a. Solar energy is received in sufficient quantity to
       supply all future U.S. heat and power requirements.
   b. There are no technical barriers to wide application
       of solar energy to meet U.S. needs.
   c. If solar development programs are successful,
       . building heating could reach public use in 5 years
       . building cooling in 6 to 10 years

-21-

. synthetic fuels from organic materials in 5 to 8
   years

. electricity production in 10 to 15 years.

d. There are no significant environmental disadvantages
   to the wide use of solar energy.

The concepts of solar energy applications considered by the Panel
are listed in Table 1 and are essentially those illustrated in
Figure 1.

Table 1:   Concepts of Applications

A. Thermal energy for buildings.

B. Renewable clean fuel supplies.

   1. Photosynthetic production of organic materials
      and hydrogen.

   2. Conversion of organic materials to fuels or heat
      energy.

C. Electric power generation.

   1. Solar thermal conversion.

   2. Photovoltaic solar energy conversion.

   3. Wind energy conversion.

   4. Power from ocean thermal differences.

Concurrent to the study by the Solar Energy Panel informa-
tion on research presently under way in areas of solar energy
was requested of selected federal agencies by the Committee
on Science and Astronautics, U.S. House of Representatives [3].
The agencies queried were the National Aeronautics and Space
Administration, the National Science Foundation, the National
Bureau of Standards, and the Congressional Research Service.

-22-

Table II is a summary of federal support for terrestrial solar energy research derived from the Committee's findings. These funding levels can be compared with the recommendations of the Solar Energy Panel, as summarized in Table III. It is quickly apparent from these tables that federal support for solar energy has fallen considerably short of the levels considered necessary to achieve a significant impact on total U.S. energy needs before the end of the century.

Materials problems in the development of solar energy were only superficially considered by the Solar Energy Panel; however, they have recently been reviewed by Franklin P. Huddle of the Congressional Research Service [5]. The following quote from Mr. Huddle's statement seems particularly applicable to solar energy conversion technology at the present stage of development: "Only when materials are available with the proper range of properties to bring a proposed system concept within shooting distance of theoretical success is it time to begin work on systems designs and the pilot testing of sub-system performance." [5] The summations of materials problems given below are largely extracted from Mr. Huddle's review.

II. Thermal Energy for Buildings

Space conditioning systems are based upon the use of flat-plate collectors tilted a fixed amount toward the equator as the least costly of the possible collection devices. This type of solar collector, illustrated in Figure 2, consists of a black solar absorber surface, which is backed by thermal insulation and overlaid by two or more air-spaced glass or

-23-

SUMMARY OF FEDERAL SUPPORT FOR TERRESTRIAL
SOLAR ENERGY RESEARCH

[IN MILLIONS OF DOLLARS][1]

	FISCAL YEAR —		
	1971 (ACTUAL)	1972 (ACTUAL)	1973 (ESTIMATED)
NSF / RANN	1.20	1.60	3.80
NASA		.23	.50
TOTAL	1.20	1.83	4.30

[1]FIGURES ARE ROUNDED

TABLE III
(Ref. 4)

SUMMARY OF OVERALL PROGRAM FUNDING
[IN MILLIONS OF DOLLARS]

APPLICATIONS	SHORT RANGE R.&D. PROGRAM (3 YEARS)	LONG RANGE[1] R.&D. PROGRAM (15 YEARS)
THERMAL ENERGY FOR BUILDINGS	15.8	97.6
RENEWABLE CLEAN FUEL SUPPLY:		
PHOTOSYNTHETIC PRODUCTION OF ORGANIC		
MATERIALS AND HYDROGEN	8.0	61.5
CONVERSION OF ORGANIC MATERIALS		
TO FUELS OR ENERGY	19.0	309.0
ELECTRIC POWER GENERATION:		
SOLAR THERMAL CONVERSION	11.5	1,125.5
PHOTOVOLTAIC CONVERSION	31.9	773.0
WIND ENERGY CONVERSION	[2]12.0	[3]610.5
OCEAN THERMAL GRADIENTS	1.5	97.5
TOTAL	99.7	....

[1] INCLUDES SHORT RANGE (1st 3 YEARS).
[2] INCLUDES $8,000,000 FOR A FUEL CELL R.&D. PROGRAM.
[3] INCLUDES $93,000,000 FOR A FUEL CELL R.&D. PROGRAM.

TWO GLASS
COVER PLATES

BLACK METAL SHEET TO WHICH
1/2" TO 1" TUBING IS BONDED

INSULATION (2" TO 4" THICKNESS)

ROOF SURFACE

SHEET METAL TROUGH OR PAN
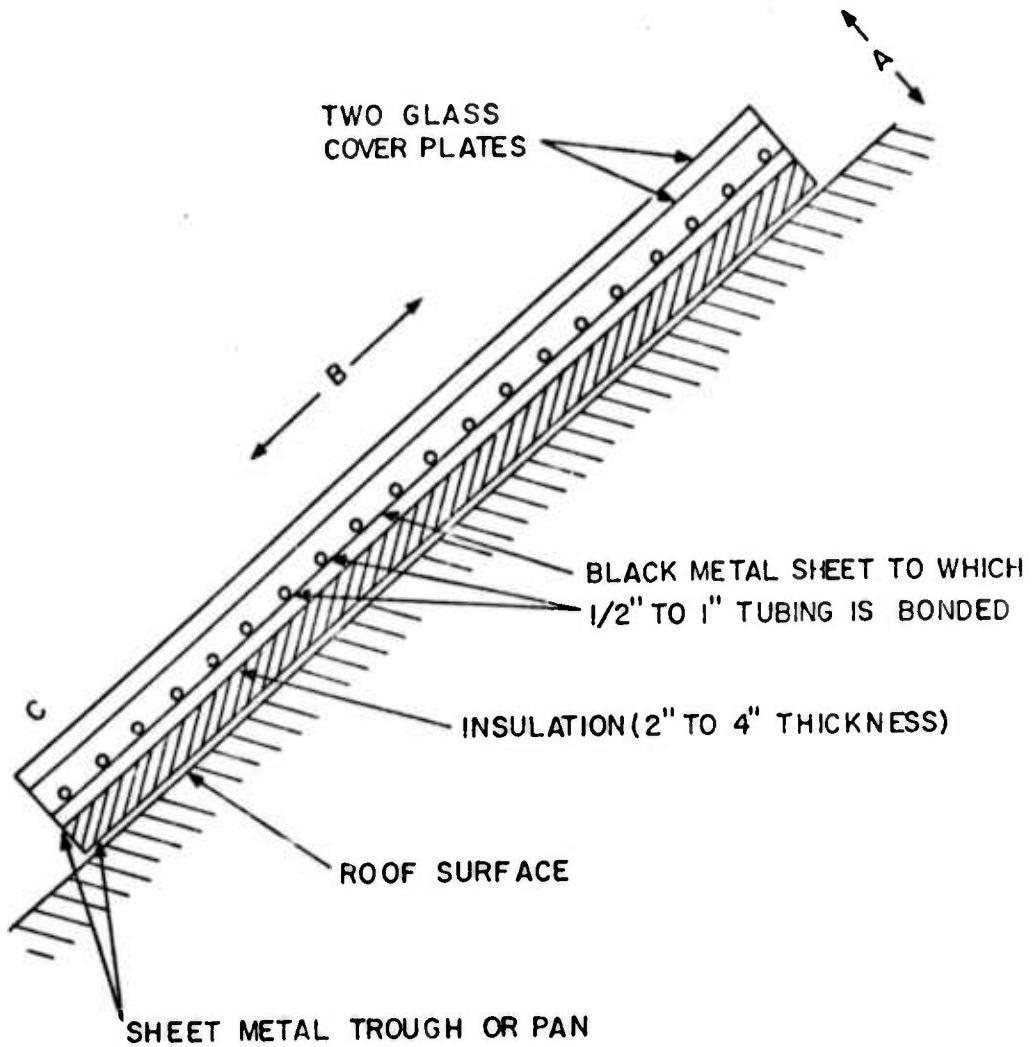
NOTES: ENDS OF TUBES MANIFOLDED TOGETHER
ONE TO THREE GLASS COVERS DEPENDING
ON CONDITIONS
DIMENSIONS: THICKNESS (A DIRECTION) 3 INCHES TO 6 INCHES
LENGTH (B DIRECTION) 4 FEET TO 20 FEET
WIDTH (C DIRECTION) 10 FEET TO 50 FEET
SLOPE DEPENDENT ON LOCATION AND ON
WINTER-SUMMER LOAD COMPARISON

FIGURE 2.   SOLAR COLLECTOR FOR RESIDENTIAL HEATING
AND COOLING. (REF. 4)

plastic cover plates to minimize convective heat losses and thereby act as a heat trap. Sensible heat is transferred from the collector plate to a gas or liquid working fluid, which passes through the collector plate tubing, is collected by a manifold system, and is finally transferred to a remote point where the sensible energy is used or stored.

The development goal for flat-plate collectors is to reduce their costs to about $1-2/ft^2 in order to bring solar space conditioning within the competitive cost range of other energy sources for building heating and cooling. Improvements in flat plate collectors may be expected in two areas [1]; (a) lowering the cost of collectors by improved integrated assembly methods; (b) increasing the wavelength selectivity of the collector surface, making it capable of achieving a much higher equilibrium temperature than an ordinary black surface.

A number of experimental "solar" houses have been constructed in recent years in order to evaluate the operating efficiency of collector and heating system designs and to establish construction and operating costs. Nearly all of these experimental systems have been installed as an additive unit to the auxiliary heating source and have employed separate controls. The achievement of economic feasibility for solar space conditioning will be best served by a systems approach, as illustrated in Figure 3, in which hot water heating, space heating, space cooling, storage, the auxiliary energy supply, and controls are integrated into a single, self-contained system. Such a system is currently being designed by the
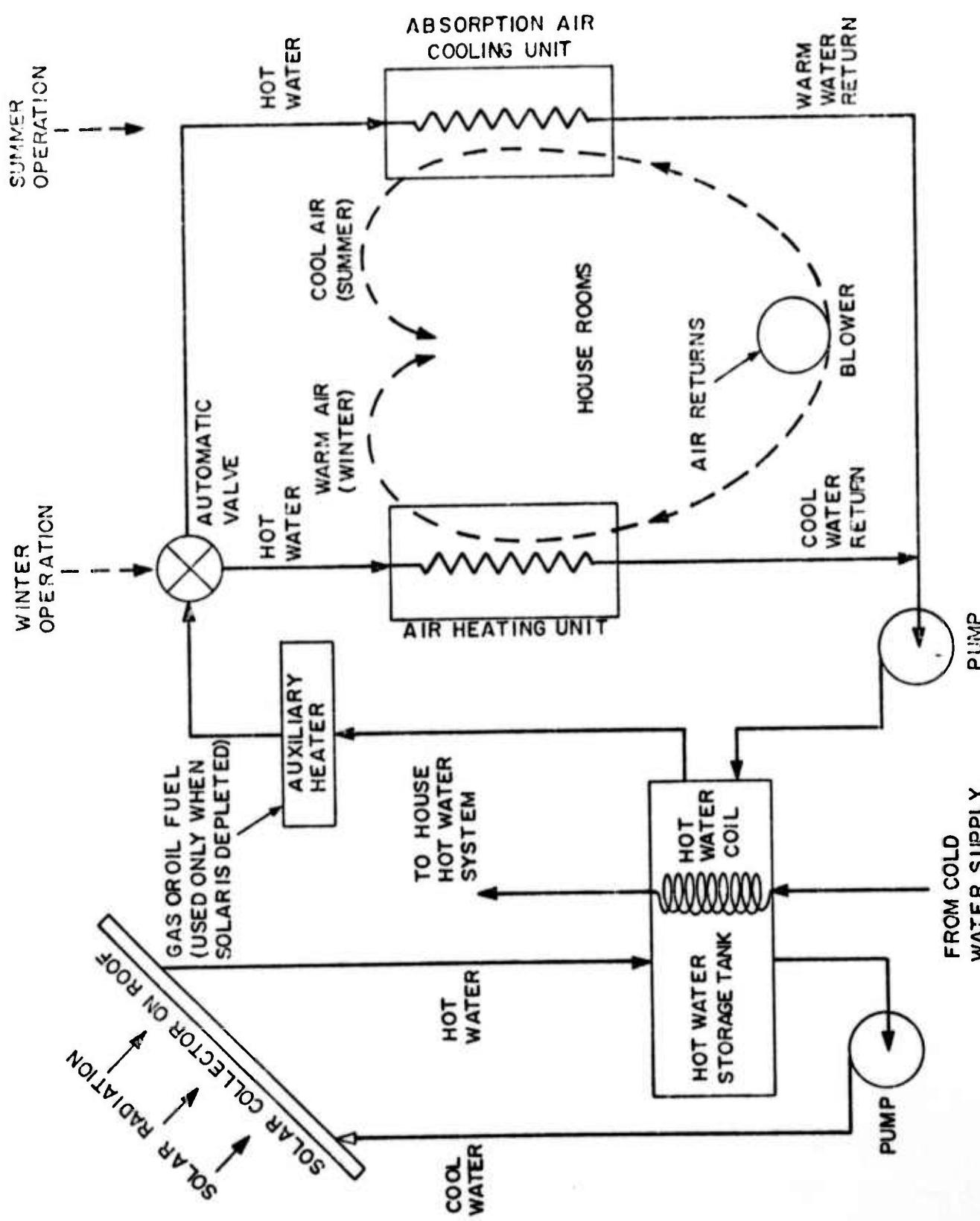
FIGURE 3. RESIDENTIAL HEATING AND COOLING WITH SOLAR ENERGY: SCHEMATIC DIAGRAM OF ONE ALTERNATIVE. (REF. 4)

-28-

A. D. Little Co. for a new building to be constructed in 1974 by the Audubon Society [6].

The addition of photovoltaic solar cells to the thermal solar collector (Figure 4) adds an additional degree of flexibility to the design of a residential solar energy system (Figure 5). In addition to total space conditioning requirements, auxiliary electrical energy is generated which can assist in reducing daytime peak demands of the local electrical utility (and reduce off-peak storage requirements) or which can be stored as chemical energy for nondaylight auxiliary energy or for battery-powered automobiles.

The materials problems associated with climate conditioning systems can be categorized as "low technology." Nevertheless, they will not be easily solved and will require painstaking development and innovative application of low-cost materials. Some of these problems are the following:

a. Integrated design for space heating and cooling, water heating, and auxiliary energy supply.

b. Reduced cost of flat plate collectors to $1-2/ft^2.

c. Selection of heat storage salts and long-lasting, corrosion-resistance containers.

d. Development of cover plate material that is

. highly transparent to visible solar radiation

. opaque to infrared radiation

. resistant to thermal cycling, heat shock, and weathering

-29-
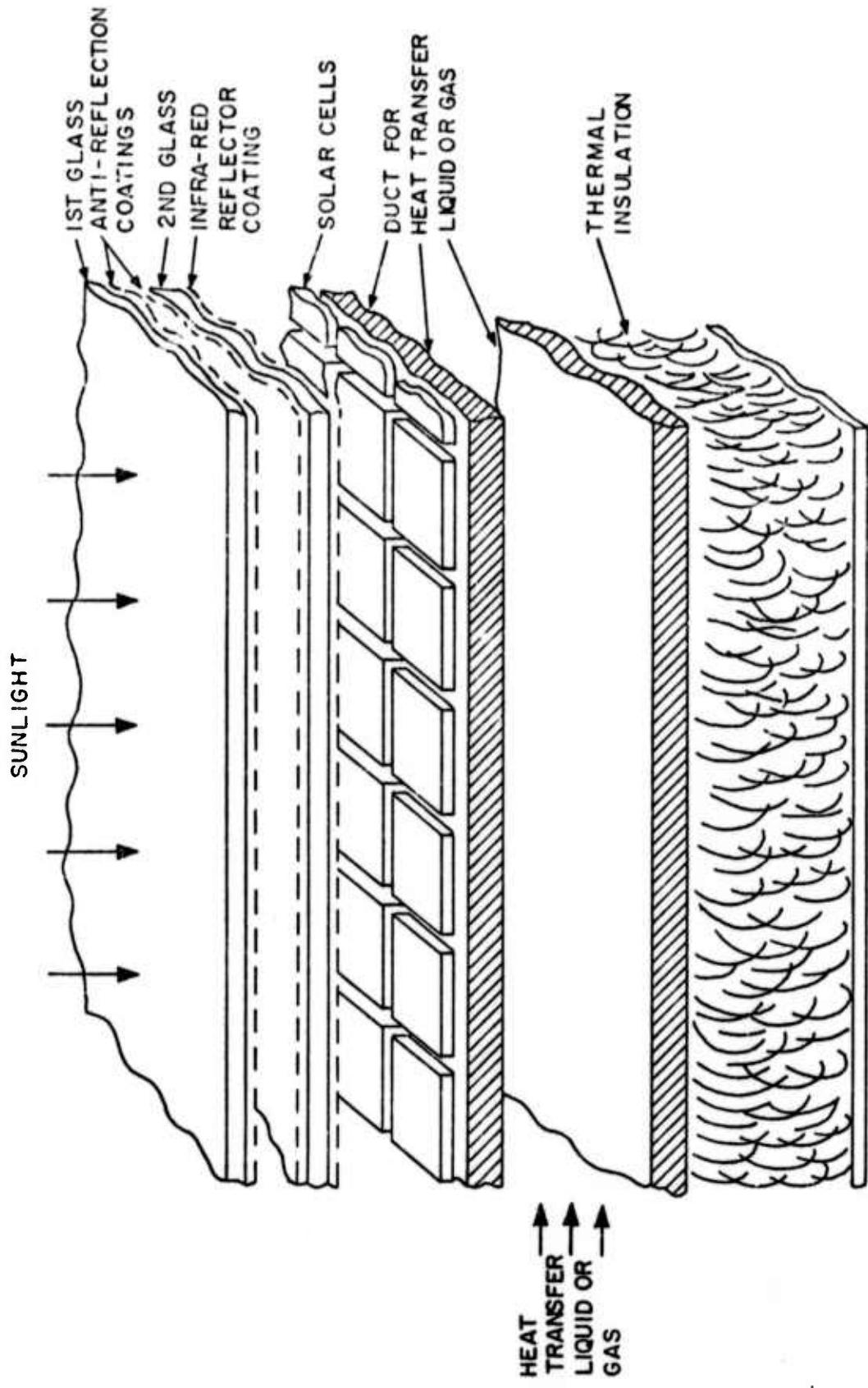
FIGURE 4: STRUCTURE OF COMBINATION THERMAL-PHOTOVOLTAIC SOLAR COLLECTOR. (REF. 4)

SUNLIGHT

IST GLASS
ANTI-REFLECTION COATINGS
2ND GLASS
INFRA-RED REFLECTOR COATING
SOLAR CELLS
DUCT FOR HEAT TRANSFER LIQUID OR GAS
THERMAL INSULATION

HEAT TRANSFER LIQUID OR GAS
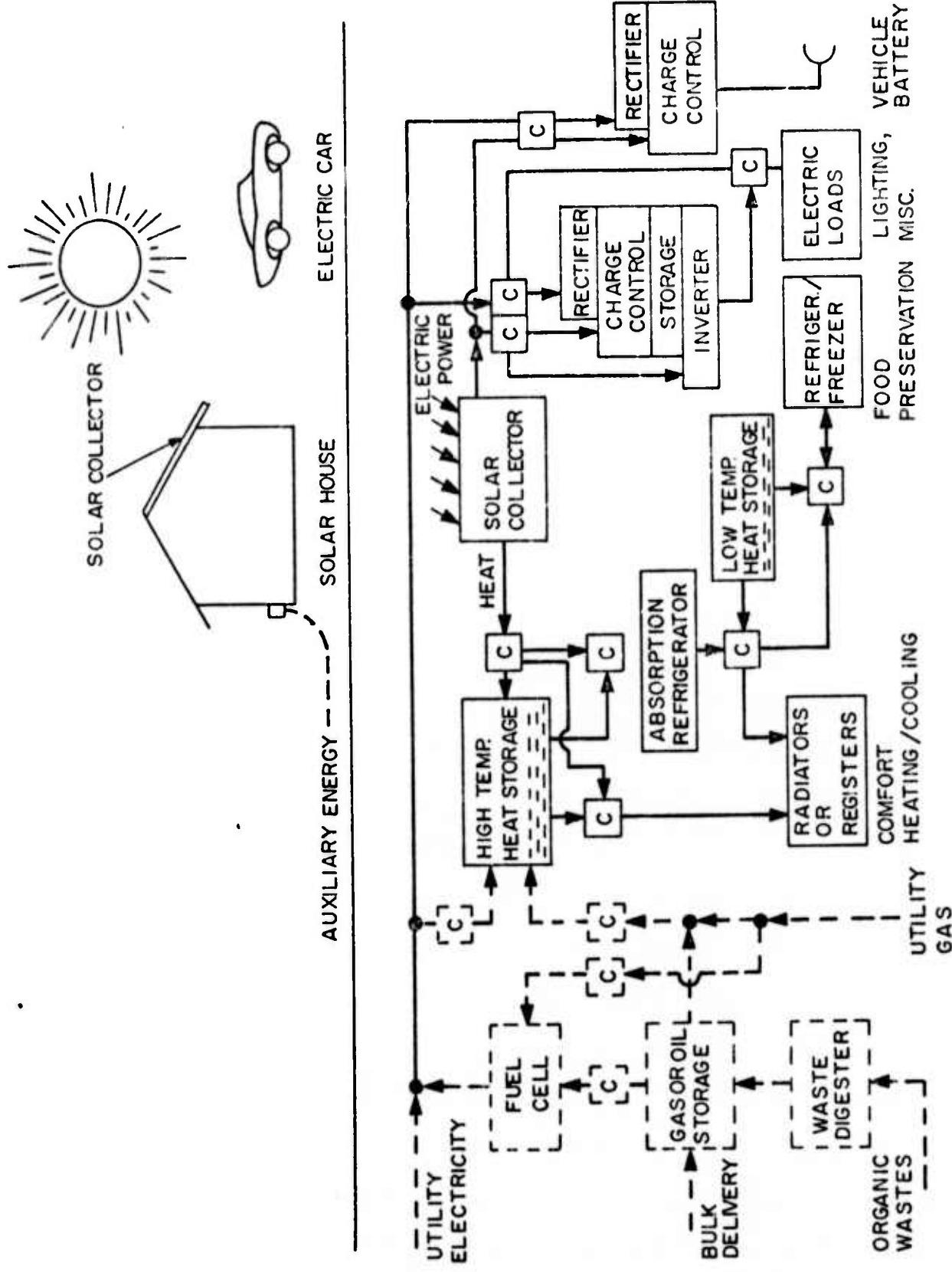
FIGURE 5. SCHEMATIC OF SOLAR ENERGY SYSTEM FOR RESIDENTIAL BUILDING (REF. 4)

. tolerant to ultraviolet light without discoloration

. compatible with sealant and joining materials

. capable of being mass produced in reliable quality
   at low prices

e. Low-cost heat exchangers, piping, and couplings.

f. Stabilization of the state of the art.

III. Renewable Clean Fuel Supplies

Although this area of solar energy technology constituted
a major portion of the Solar Energy Panel's study, it is
considered peripheral to the main interests of the ARPA Materials
Research Council and will be outlined only briefly. The follow-
ing methods for producing renewable clean fuels were considered
by the Panel:

a. Combustion of organic materials.

b. Bioconversion of organic materials to methane.

c. Pyrolysis of organic materials to gas, liquid, and
    solid fuels.

d. Chemical reduction of organic materials to oil.

These processes are schematically illustrated in Figure 6, and
the process requirements for chemical reduction, pyrolysis,
and fermentation of organic matter are compared in Table IV.

Fermentation not only is the least demanding process from
the standpoint of pressure and temperature but also produces a
high Btu gas containing from 50 to 70% methane. However, the
process holdup times for this process are relatively long,
necessitating large tank volumes. Solid waste pyrolysis
requires high process temperatures, 500-900°C; however, the
process technology is well advanced, and commercial-scale

-32-

FIGURE 6
(Ref. 3)

CLEAN RENEWABLE FUEL FROM SOLAR ENERGY

-33-
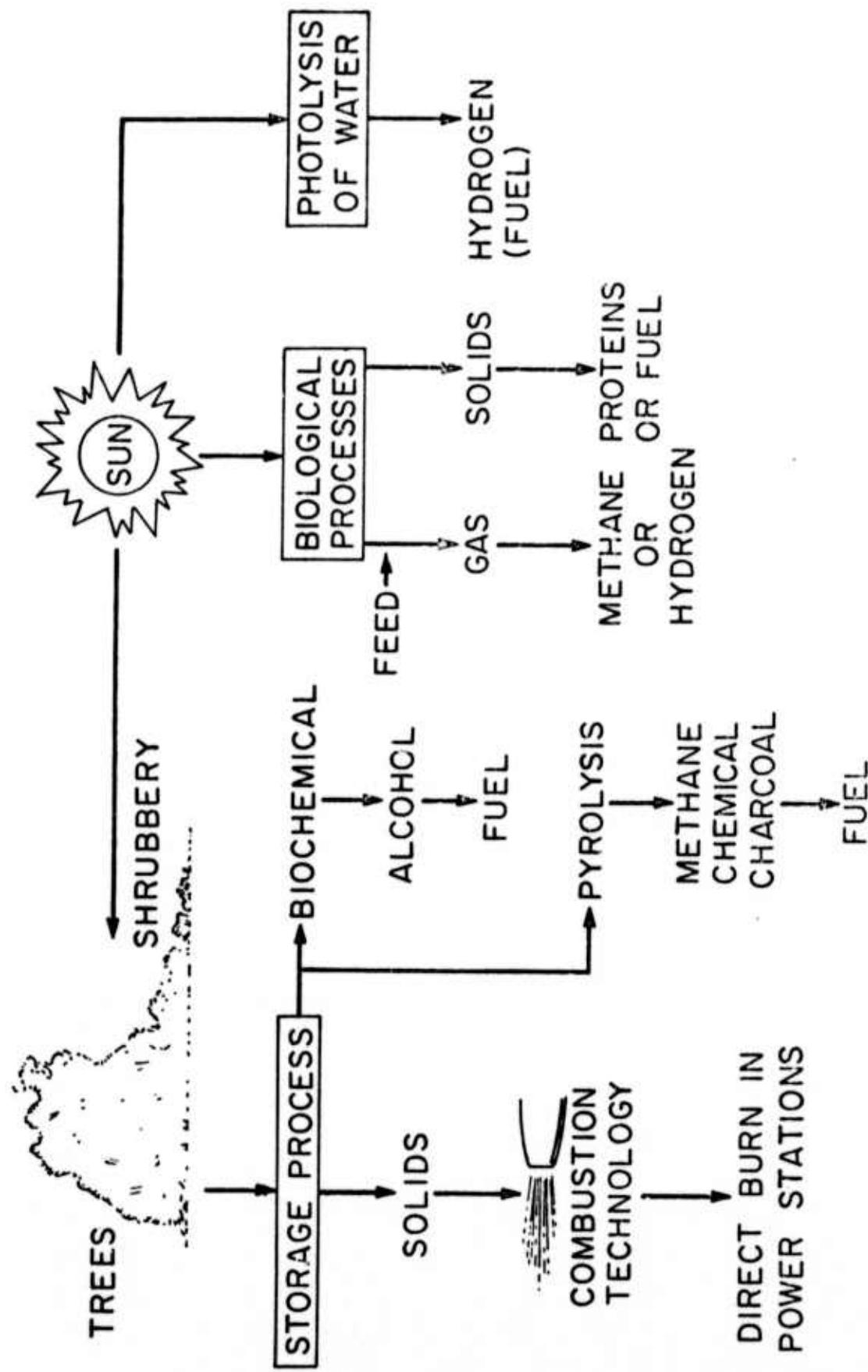
TABLE IV

Comparison of Methods for Conversion of Solid Wastes to Clean Fuel (Ref. 4)

	Chemical Reduction	Pyrolysis	Fermentation
Process Requirements			
Form of feed	Aqueous slurry (15% solids)	Dried waste	Aqueous slurry (3-20% solids)
Temperature	320°-350°C	500°-900°C	20°-50°C
Pressure	2,000-5,000 psi	Atmospheric	Atmospheric
Agitation	Vigorous agitation	None	Slight
Other	Uses CO	None	None
Future of Product	Oil	Oil and Char	Gas
Yield (percent of original material)	23%	40% oil; 20% char	20%-26% (maximum)
Heating value	15,000 Btu/lb.	12,000 Btu/lb. oil* 9,000 Btu/lb. char*	23,800 Btu/lb.
Percent of original heat content recovered in product (assume 8,000 Btu/ lb. dry waste)	37% (corrected for CO use) 65% anticipated	82% (60% if char not included)	60% (77% maximum)

*All of gas and 1/3 of char used to supply heat.

-34-

units are being installed in the Northeast [6] for demonstration testing with urban solid wastes. In the chemical reduction process, organic materials are subjected to elevated temperature and pressure in the presence of water, carbon monoxide and catalyst and are partially converted into oil having a heating value of about 15,000 Btu/lb. This process has the advantages of being continuous and requiring relatively short residence times (1 to 2 hours); however, high temperatures and pressures complicate materials transfer into and out of the system and require the use of a high-temperature pressure vessel.

Many of the unresolved materials problems associated with photosynthesis and bioconversion systems are related to resource management and harvesting of the organic biomass and nutrients. Some of these are summarized below [5]:

a. Maximization of bioproductivity of proper nutrients, environment maintenance, and genetic engineering.

b. Development of low-cost, long-life hardware for efficient harvesting of biomass.

c. Systems developments for converting biomass into usable fuels by fermentation and combustion.

d. Development of technology for drying of biomass.

e. Extraction of sulfur from combustibles.

f. Maximization of solar energy capture by symbiotic relationships between various combinations of solid waste and biomass.

g. Increasing the biomass yield of agriculture without increasing food costs.

-35-

h. Comparing the utilities of biomass conversion into methane, thermal energy, or synthetic petroleum.

i. Protecting process equipment against corrosive action of biological materials, combustion products, seawater, and hot solutions.

In addition to materials problems, a number of broad-ranging questions related to environmental control, ecological imbalances, and public acceptance of using highly productive land or waterways for biomass production for fuel must be resolved before these methods of solar energy conversion can make a significant impact on projected energy needs.

IV. Electric Power Generation

A variety of approaches have been suggested for using solar radiation in central power generation. Among the schemes studied by the Solar Energy Panel are the following:

a. Thermal conversion.

b. Photovoltaic.

c. Wind energy conversion.

d. Ocean thermal gradients.

The first two of these schemes can be classified as "technological collection" and the latter two as "natural collection." The various options for converting solar energy to intermediate forms of energy and finally to electrical energy are illustrated in Figure 7. Most of these options involve energy storage either in the form of heat or chemical fuel, and some require the storage and transportation of hydrogen.
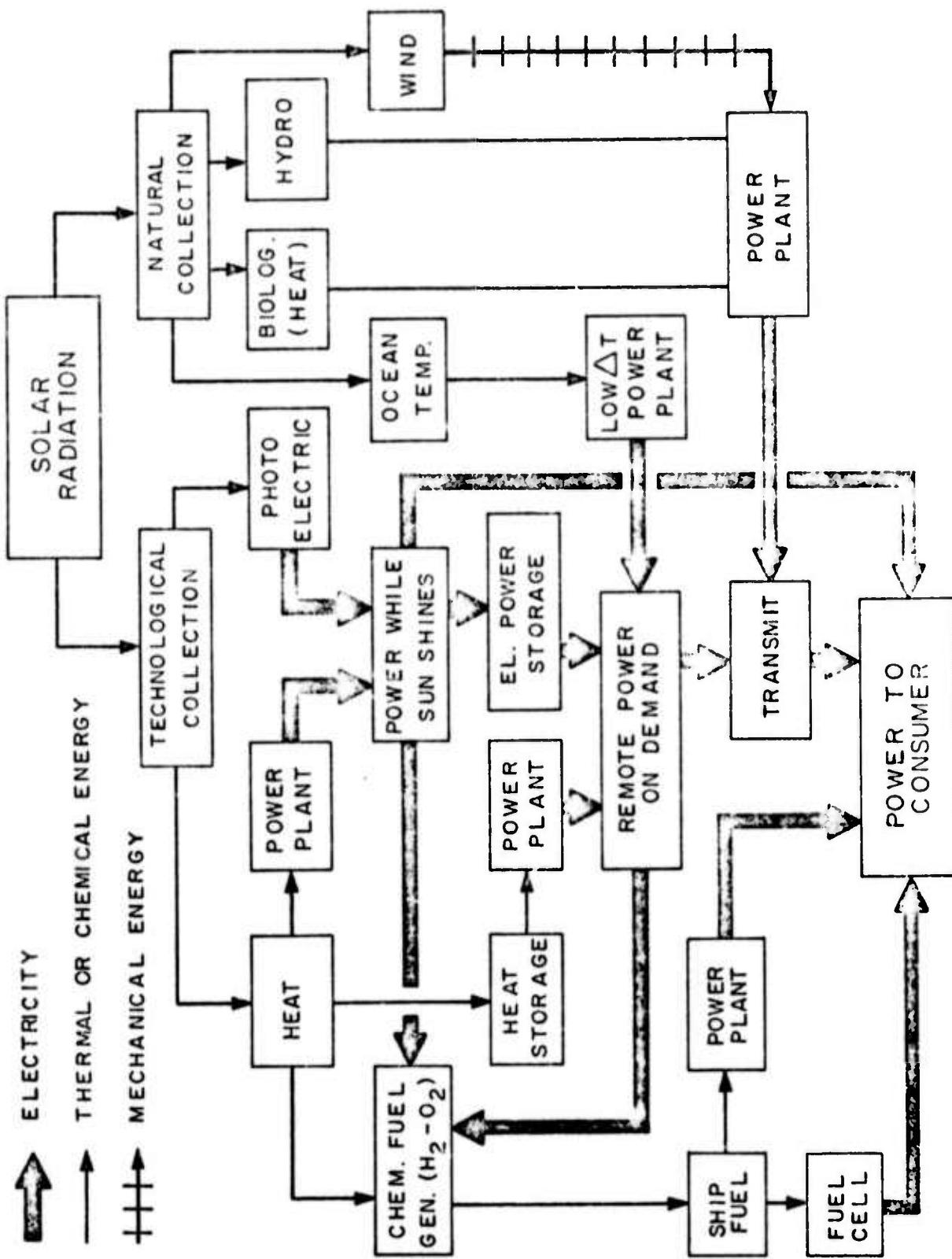
FIGURE 7. CONVERSION OF SOLAR ENERGY TO ELECTRICITY. (REF. 4)

A. Thermal Conversion

Several attempts, starting from the last century, have been made to generate power from the sun by thermal conversion. The last and perhaps most significant effort was the Russian study at Tashkent in the 1950's, which has since been abandoned [1].

Recently, however, Adam and Marjorie Meinel of the University of Arizona have developed a concept for a solar power farm, which has stimulated the interest of several investigators to examine various forms of the basic concept. The general claims of the Meinels are as follows [7]:   (1) thermal conversion of solar energy into electrical power at efficiencies approaching 30% is possible using current technology; (2) economics of solar power appear to be comparable to the generation of power today using natural gas as fuel; (3) solar power production has the potential of sustaining the entire power needs of the United States within reasonable uses of land area; and (4) the technology could be developed by the first half of the 1980's.

Hottel and Howard [1] have questioned the Meinels' claim of a potential conversion efficiency of 36% on the grounds that it assumes overly optimistic optical properties and lifetime performance of selective coatings; it does not account for the degradation in optical transmittance in glass piping due to weathering; and it ignores the vast amount of pumping power required to circulate heat transfer fluids over large distances.

-38-

Hottel and Howard find that an overall efficiency of 11% is probably more reasonable [1].

Apart from the technology required to increase the operating temperature of the solar collector element, a thermal storage subsystem will be required in order to satisfy energy generation deficiencies during periods when the sun is not shining. A chemical storage capability also affords an opportunity for converting surplus solar power generated during the summer months into hydrogen or a hydrocarbon fuel that can be burned in a conventional boiler to make up the winter deficiency in sunlight. Optimum design of these energy storage subsystems is required to minimize the total amount of solar collector surface area required for a fixed, steady electrical generating capacity. The general relationships of both the thermal storage and chemical storage subsystems to the Meinel solar farm concept are shown schematically in Figure 8. The allowable construction budget for such a farm to produce power at a cost of 5.3 mills/kwh at a conversion efficiency of 25% and at a site having 330 clear days/year has been estimated by the Meinels at $60/square meter [7].

A typical Meinel collector panel is illustrated in Figure 9. Focused sunlight initially concentrated by a cylindrical mirror enters an evacuated glass pipe through a limited transparent region. Since the remainder of the internal surface of the glass vacuum pipe is silvered to produce a high reflectivity, sunlight entering the pipe will impinge on a steel pipe containing a selective coating having a high absorptivity to

-39-

FIGURE 8. The Meineis' Proposal for a Solar Energy Form (Ref. 7)

SOLAR POWER FARM COLLECTING AREA

THERMAL STORAGE

CLOSED-LOOP CHEMICAL WINTER RESERVE FUEL

POWER TURBINE

CONDENSER

SUMMER EXCESS POWER

POWER OUTPUT

-40-
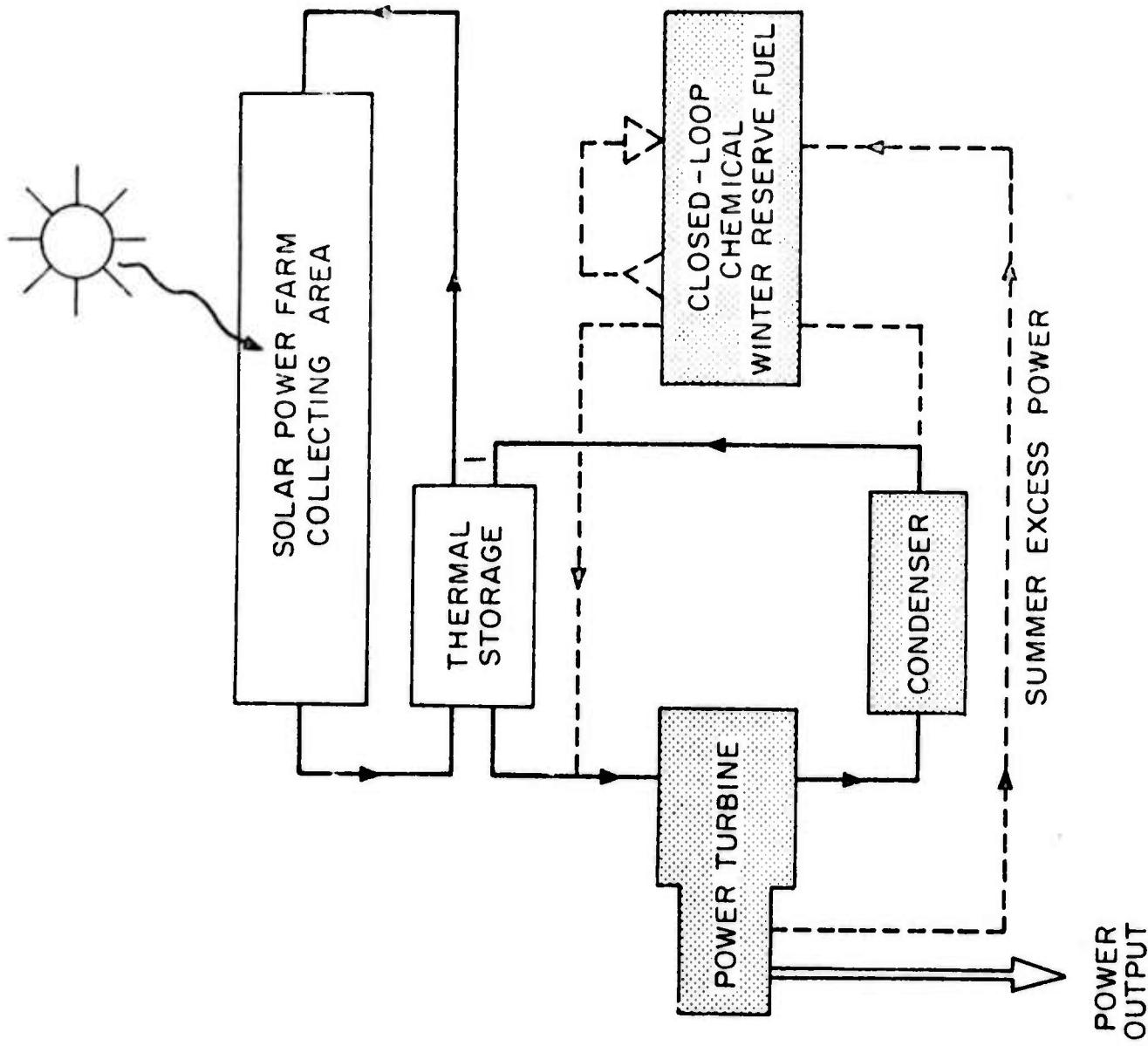
CROSS SECTION DIAGRAM OF A TYPICAL COLLECTOR PANEL USING A CYLINDRICAL REAR-SURFACED MIRROR AS THE CONCENTRATOR

SUNLIGHT

GLASS VACUUM PIPE (SILVERED)

CLEAR WINDOW

MIRROR CONCENTRATOR (CYLINDRICAL)

SELECTIVE COATED STEEL PIPE
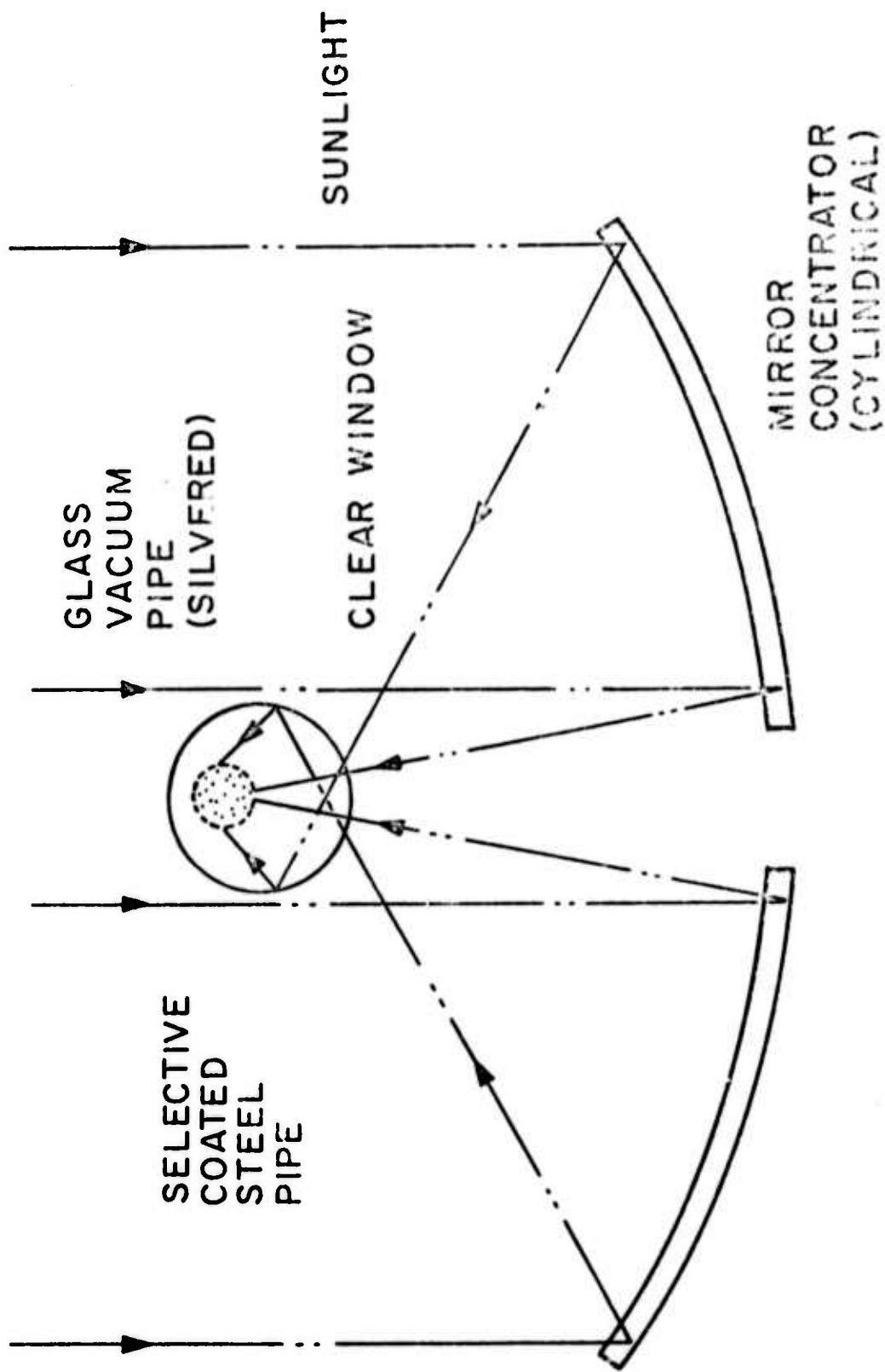
visible sunlight but a low emissivity in the infrared spectrum. Under no convection heat losses from the evacuated enclosure and no extraction of the absorbed energy, the steel pipe would reach a steady-state temperature or about 900°C [7]. A method for extracting heat economically, reliably, and safely with either liquid or gaseous working fluids is one of the major engineering problems that must be solved.

A major materials problem affecting the maximum outlet temperature from the collector panel is the development of a long-lasting, high-efficiency, economical selective coating. The relationship between the performance curve and physical behavior for a selective coating is shown in Figure 10. The outer layers of the coating, which are transparent in the infrared region, consist of both outer, nonreflecting layers that improve collection efficiency and an absorbing layer that is opaque to sunlight. The inner layer between the absorbing layer and the steel substrate consists of a highly reflective metallic coating, which has a low infrared emissivity and has the function of trapping heat within the pipe. The overall coating thickness is about 0.00001 in. thick and has an overall efficiency given by the ratio a/e, the absorptivity in the visible divided by the emissivity in the infrared. The materials selected for these coatings must not only provide a high value of this ratio but must also resist interdiffusion and degradation at service temperatures to about 500°C for lifetimes of the order of 40 years. Several coating types have

-42-

FIGURE 10
(Ref. 7)

RELATIONSHIP BETWEEN THE PERFORMANCE CURVE AND
PHYSICAL BEHAVIOR FOR A SELECTIVE COATING

-43-
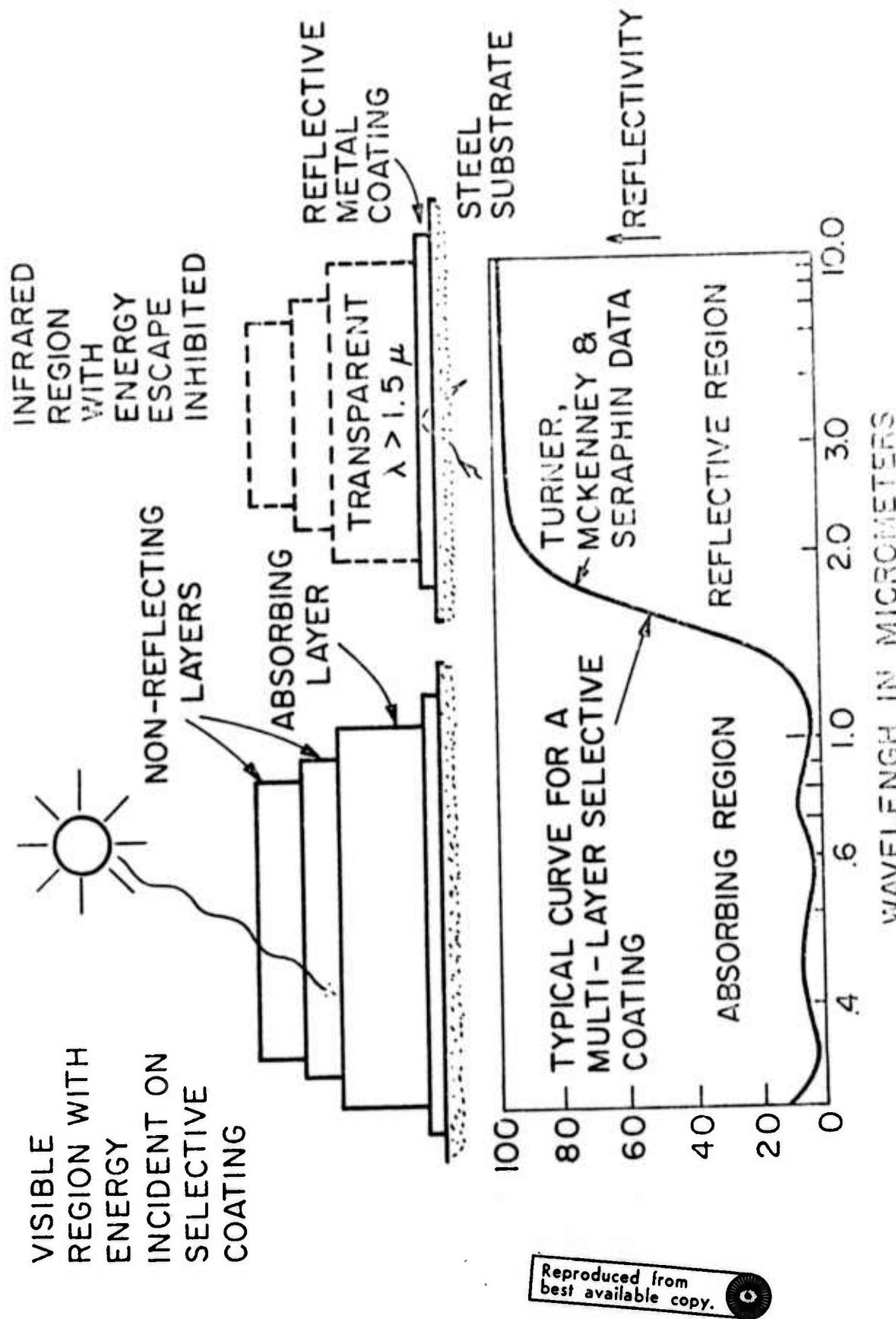
been developed using silicon as the absorbing layer and refractory metals for the reflective layer, and these exhibit absorptivities in the visible ranging from 0.75 to 0.88 and a/e ratios ranging from 7 to 10 at 500°C [7].

The operating temperature of a collector panel is determined by both the optical concentration of the sunlight, X, and the selectivity, a/e; and the product of these parameters should be about 100 to achieve desirable conversion efficiencies. This figure of merit can be achieved by either combining a high degree of optical focusing with a nominal, inexpensive coating or a less efficient concentrator system with a high degree of coating selectivity. A considerable amount of uncertainty exists in determining an optimum combination of these factors. Furthermore, a number of possible schemes have been proposed employing cylindrical parabolas or paraboloids to focus solar energy. However, most suffer from two grave weaknesses: a prohibitive cost of the support and tracking mechanism for the focusing optics and the loss of diffuse or sky radiation that constitutes a significant fraction of the total energy from the sun. Among the materials problems that are inherent in this approach to solar power technology are the following:

(1) Optimum thickness of coatings for efficient capture of solar energy.

(2) Low-cost production methods for applying coatings.

(3) Effective life and maintenance of preferred coatings in actual service.

-44-

(4) Feasibility of a large network of vacuum-tight, ceramic tubing.

(5) Stability of thin films under frequent thermal cycling.

(6) Efficient insulation of heat storage system.

(7) Selection of heat storage materials.

(8) Reliability of selective coating performance at high temperatures.

(9) Fabrication, cost, and durability of concentrators (if used).

(10) Compatibility of heat pipe materials to working fluids.

B. Photovoltaic

Under the strong impetus of the space program, a limited number of photovoltaic materials have been brought into an "adolescent" stage of development for solar cell applications under NASA and Air Force sponsorship. Silicon, a homojunction material used for spacecraft solar power generation, has a theoretically achievable conversion efficiency of about 25%. In comparison, about 11-12% efficiency has been achieved in commercially produced, single-crystalline silicon; and about 18% has been achieved in laboratory-prepared material.

Because of the stringent reliability and quality control requirements imposed by space applications, solar cells are currently produced by "cottage" industry techniques involving hand selection and assembly methods. Accordingly, silicon solar cells currently cost about $200-300/watt exclusive of support hardware and control systems. A nearly one-hundred-fold cost reduction will be required in order to make electrical power production from such solar cells competitive with

currently conventional fossil and nuclear power plants [4].
However, the extensive availability of silicon as a natural
resource in quantities suitable for large-scale power produc-
tion and the substantial cost reductions projected (nearly a
factor of five or more) over the near term by obvious improve-
ments in processing methods provide a favorable long-term
outlook for photovoltaic power production.

Other homojunction semiconductors, such as CdTe, GaAs,
and InP, have also received attention for solar cell applica-
tions; however, performance characteristics in terms of
efficiency and resistance to degradation are not so well under-
stood or developed as in the case of silicon. Furthermore,
the limited availability of tellurium, gallium, and indium
is probably the major detrimental factor in the eventual
application of these materials for other than small or
specialized power systems.

Among possible heterojunction solar cells, Cu-CdS has
received the greatest attention and process development. Since
Cu-CdS cells can be manufactured for about 1/30 as much per unit
area as silicon cells with current technology [1], such cells
have enormous economical significance. However, these cells
have achieved only 5% efficiencies to date and suffer from
significant photodegradation over a relatively short time
period. Additional knowledge into the physics and metallurgy
of heterojunction cells is necessary to determine their full
performance potential.

Finally, Schottky barrier diodes and organic semiconductors

-46-

have also been proposed for photovoltaic cells; however, the theory and experimental data for these materials are limited. The characteristics of photovoltaic materials will be brought into sharper focus during these discussions by Joseph Laferski, Roy Kaplow, and others.

Because of the ubiquitous nature of sunlight, photovoltaic cells offer a high degree of dispersion in the production of electrical power. In terrestrial applications, the scale of application is dependent primarily upon capital cost constraints and the availability of suitable energy storage systems to satisfy steady power demands. However, the flexibility and dispersion inherent in photovoltaic direct conversion systems offer cost tradeoffs against costly, conventional power transmission and distribution networks.

The use of photovoltaic cells in combination with rooftop flat plate collectors to supply auxiliary electrical power for buildings has already been touched upon. Such a symbiosis must take into account the inverse relationship between photocell operating efficiency and temperature and the need to remove the thermal energy resulting from inefficient photon-induced electron excitation processes that do not contribute to the current output of the cell. Some feasible arrangements for combined collectors will be described by Roy Kaplow.

The Satellite Solar Power Station (SSPS) proposed by Peter E. Glaser [8] has the principal advantage of constant production of electrical power without the need for an energy storage system. Such a space station scaled to produce 1,000 MW of

-47-

electrical power is illustrated in Figure 11. The overall system consists of both an orbiting solar energy conversion station in synchronous Earth orbit and an Earth-based receiving antenna. Huge mirror concentrators focus sunlight onto two solar panel arrays, each 4 km on a side. The d.c. electrical current from the solar panels drives a 1 km-dia. microwave antenna which generates and transmits a microwave beam to the Earth-based ground receiving station. Here, the microwave energy is reconverted into electrical power for the consumer. Considerable skepticism about the practicability and economic feasibility of this scheme has been expressed, and there is concern about the environmental effects of microwave transmission. However, a potential conversion efficiency in excess of 90% of the electrical power delivered from the solar cells and the currently advanced stage of microwave technology commended this option to a detailed feasibility study by a consortium of four companies: A. D. Little; Heliotek, Division of Textron Industries; Grumman Aircraft Corporation; and Raytheon. This study showed that cost reductions on the order of 2-5 times of those current foreseen are required to achieve economic feasibility. Furthermore, key technology needs in low-cost solar cells, light-weight structures, and efficient, safe, microwave transmission were identified.

Substantial advances and some breakthroughs in the development, characterization, and processing of photovoltaic materials will be required in order to produce abundant amounts of electrical power at a cost that will benefit other than the most

-48-
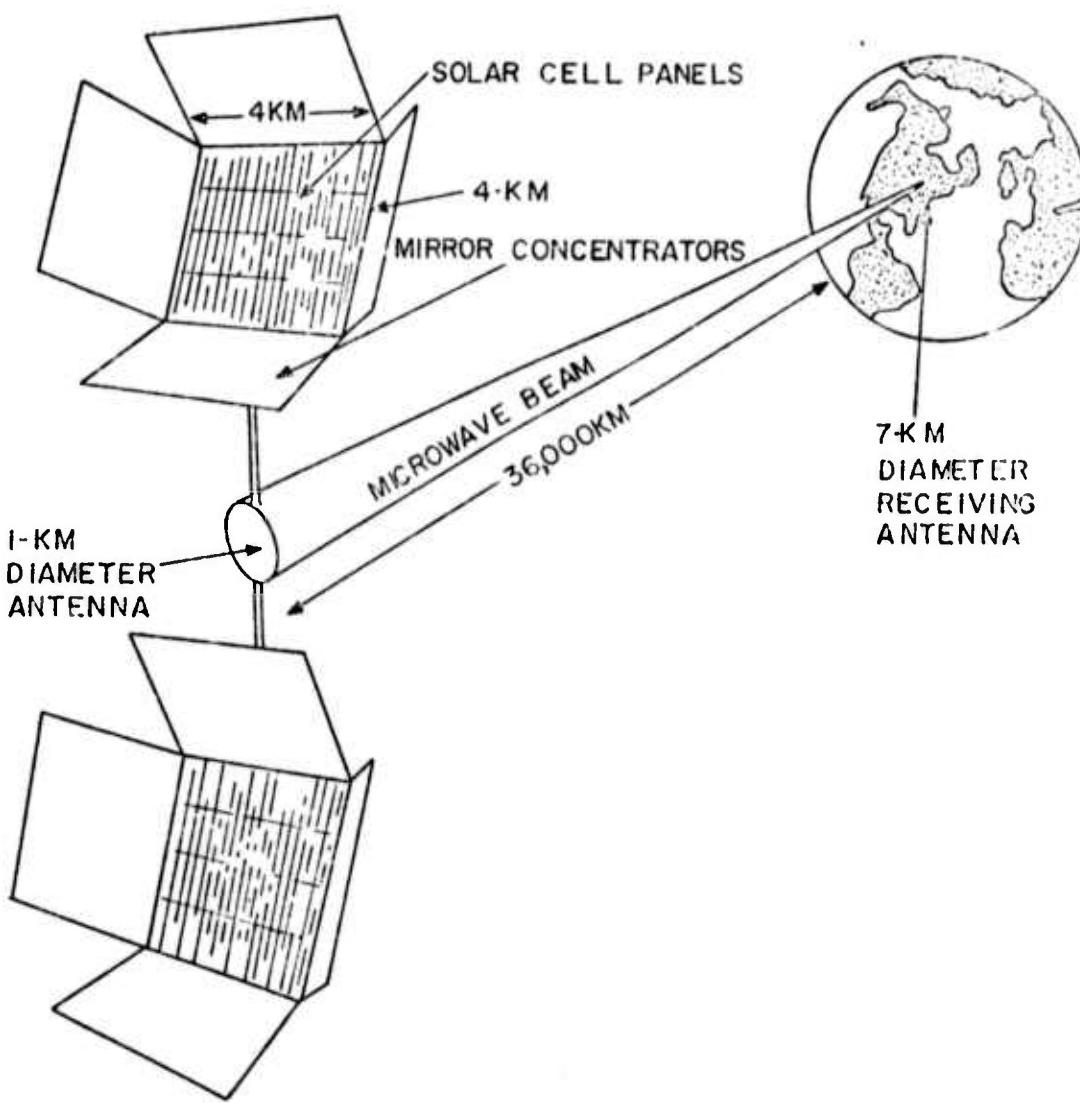
FIGURE II   SPACE STATION CONCEPT TO PRODUCE 10,000 M.W.
             (REF. 4,8)

technically and economically advanced nations. Among the materials problems that can be cited are the following. Technical advances are required in:

(1) Increased life of semiconductor material in the hot environment.

(2) Increased efficiency per area of cell.

(3) Cost reduction to 1/100 of present manufacture costs. (Improve cost/effectiveness of high-purity silicon from \$100,000/kw to \$1,000/kw).

(4) Advanced process technology (vacuum evaporation, sputtering, electron beam ion plating, chemical vapor deposition).

and in space:

(5) Limiting vapor pressure of materials (especially metals).

(6) Hardening against radiation damage.

(7) Tenfold reduction in weight/kilowatt of the space array.

C. Wind Energy Conversion

The winds and oceans represent vast natural reservoirs of energy collected from the sun. Properly harnessed wind power can supply a significant fraction of the world's electrical power demand. Wind turbines are currently in use on a small scale throughout the world, and one large-scale experimental aeroelectric turbine with a peak generating capacity of 1,250 kw operated for 23 days on the electrical grid of the Central Vermont Public Service Corporation in 1941 [2].

A block diagram of a wind conversion system proposed by

Professor W. E. Heronemus of the University of Massachusetts is illustrated in Figure 12. In this system, thousands of wind turbines driving a.c. generators would be located off the New England coast. Electrical power would be transmitted by way of cables along the seabed to central electrolyzer stations where it would be either converted to hydrogen and oxygen or distributed directly to electrical consumers. Hydrogen, stored either cryogenically ashore or in deep-water, pressure-balanced tanks would provide chemical storage for periods of low wind velocity. This hydrogen would either be reconverted into electrical power at reversible electrolyzers at the central station or transmitted through distribution pipelines to dispersed fuel cell generating stations. The materials problems associated with this scheme are principally those associated with fuel cell, electrolyzer, and generator development. Consequently, this method of energy conversion will be a principal beneficiary of current advances in high field strength magnets and in fuel cell electrode materials. Although past technology has limited the maximum size of the generator to a range of 2,000-6,000 kw, new magnet technology should permit a severalfold increase in the size of an individual unit.

D. Ocean Thermal Gradients

The ocean serves as both a vast collector and storage reservoir for solar energy. Between the Tropics of Cancer and Capricorn, the surface temperature of the oceans reaches a steady-state temperature of 25°C, while at lower depths, as shallow as 1,000 meters at some locations, glacial melt migrating to the equator from the polar regions provides a nearly infinite
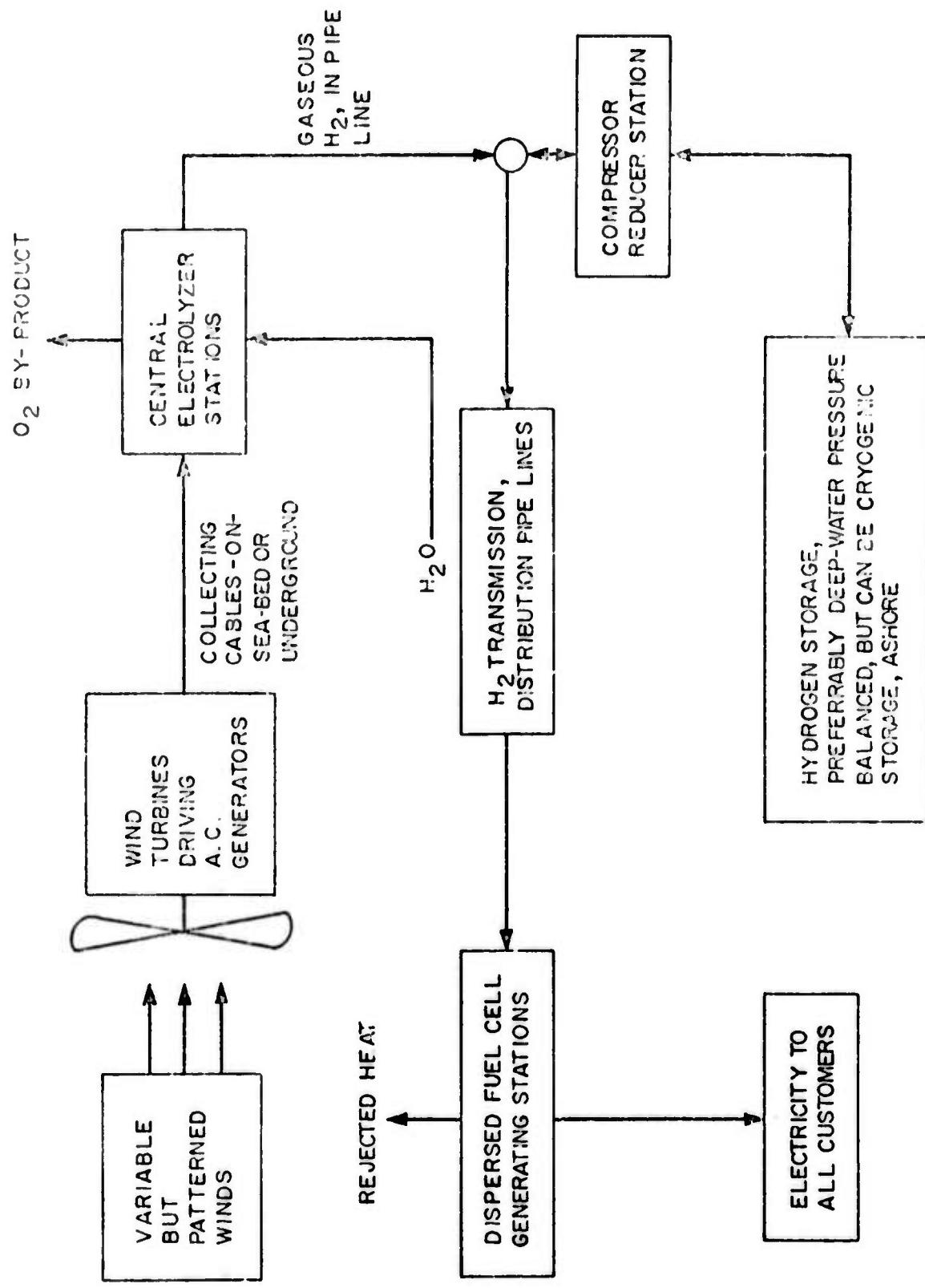
FIGURE 12. BLOCK DIAGRAM OF ONE PROPOSED WIND CONVERSION SYSTEM. (REF 4)

heat sink at about 5°C. Both the hot surface water and the cold deep water are replenishable by solar energy.

Jacques D'Arsonval, a French physicist, first proposed extracting power from a heat engine operating from ocean thermal gradient in 1881, and George Claude demonstrated a 22-kw system in Cuba in 1929. However, the Claude system was an economic failure because it used seawater, which has a low vapor pressure, as the working fluid. More recently the French built two systems of 3,500-5,000 kw capacity in 1950 for use in the Mediterranean Sea and off the Ivory Coast in Africa.

In 1964, Hilbert Anderson and James Anderson of York, Pennsylvania, patented the system shown schematically in Figure 13. This system features a submersed boiler and condenser to take economic advantage of the neutral balance between the seawater's hydrostatic pressure and the vapor pressure of the working fluid. Both ammonia and propane have been considered as the working fluid, and in the case of propane a pressure balance for the boiler operating at $\sim$20°C would be reached at a depth of 280 ft. and for the condenser operating at $\sim$10°C at a depth of about 155 ft. The Andersons estimate that the maximum possible efficiency would be about 5%, and the actual efficiency would be about 2 or 3%. Furthermore, they show that a 100-MW plant would produce about 60×10^6 gallons of fresh water per day if the hot water effluent from the boiler were degassed and passed through a vacuum evaporator and if the water vapor were condensed by the flow of cold water coming from the generating plant.

ELECTRIC POWER FROM OCEAN ΔT

GULF STREAM

TURBINE

GENERATOR

BOILER

82°F

79°F

CONDENSER

49°F

42°F

POTENTIAL
ALL 1985 ELECTRICAL
NEEDS WITH < 0.3°F
DROP IN GULF STREAM

TECHNOLOGY
SEA-WATER COMPATIBILITY
COLD WATER DUCT
COMPACT HEAT EXCHANGE
FLUID DYNAMICS
TURBINE
GENERATOR
RELIABILITY
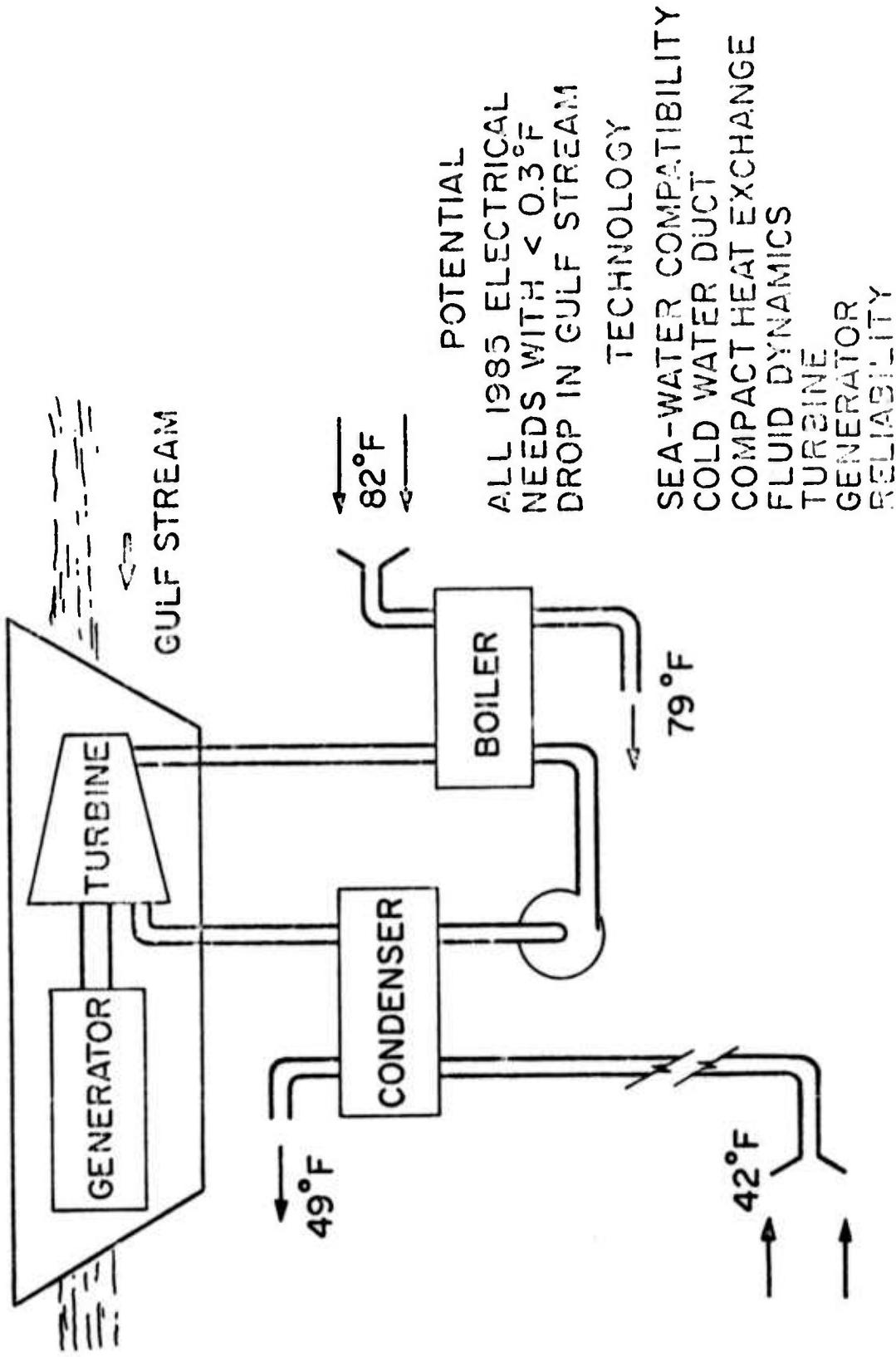
In spite of the low operating efficiency, the energy available from ocean thermal gradients is enormous, and no special collectors or energy storage systems are required. However, there are a number of difficult technology problems that must be solved, such as the following:

1. A cold-water duct about 30 feet in diameter and 2,000 feet in length that has sufficient structural rigidity and anchoring to withstand ocean current flowing in opposite directions at different depths must be designed.

2. A working fluid that has a high vapor pressure and good heat transfer characteristics at the system operating temperatures must be selected to minimize the size of the turbine, boiler, and condenser.

3. The heat exchangers must be especially designed to minimize thermal impedance across the heat transfer surfaces. Large heat transfer surfaces are required to provide heat fluxes nearly ten times those of more efficient fossil fuel boilers. Furthermore, the heat exchanger walls must not only resist fouling but must prevent the working fluid from coming in contact with seawater and causing damaging corrosion reactions. Since the boiler and condenser are submersed, the heat exchanger walls can be made quite thin.

4. The plant must be compatible with the ocean and resist corrosion, adverse weather conditions, and the clogging of ducting by debris, fish, etc.

5. A satisfactory method must be provided for transmitting energy from the plant to shore.

6. Precautions must be taken to minimize the thermal mixing
    of the boiler intake stream with the condenser outflow
    stream, which would significantly lower the overall plant
    operating efficiency.

Some of these problems, and especially those associated
with the design optimization of the heat exchangers, will be
discussed in some detail by Clarence Zener.

V. Status of Solar Utilization Techniques

The present status of solar, as determined by the NSF/NASA
Solar Energy Panel [4], is reflected in Table V. Solar water
heaters are already commercially available, and the technical
and economic feasibility of building heating is being demon-
strated by several experimental buildings within the United
States and elsewhere. It is expected that building solar heating
systems will reach commercial readiness in the near future and
that the technical status of building cooling and combined
systems will advance rapidly within the next five years.

The solar production of fuels appears from Table V to be
at a more advanced stage of development than the other techniques.
This is particularly apparent in the availability of full-scale
demonstration systems. However, the problems in producing and
harvesting various organic forms as noted previously stand in the
way of demonstrating economic feasibility and commercial readiness
of fuel generating plants.

The least developed solar utilization technique is electric
power generation, and yet it is this of the various solar utiliza-
tion techniques that has been most widely discussed as the
ultimate source of an inexhaustible energy supply. Substantial

-56-

TABLE V

Status of Solar Utilization Techniques (Ref. 4)

Technique	Research	Development	Systems Test	Full-Scale Demonstration	Model Plant	Commercial Readiness
Thermal Energy for Buildings						
Water Heating	X	X	X	X	X	X
Building Heating	X	X	X			
Building Cooling	X	X				
Combined System	X	X				
Production of Fuels						
Combustion of Organic Matter	X	X	X	X		
Bioconversion of Organic Materials to Methane	X	X	X	X		
Pyrolysis of Organic Materials to Gas, Liquid, and Solid Fuels	X	X	X	X	X	
Chemical Reduction of Organic Materials to Oil	X	X	X			
Electric Power Generation						
Thermal Conversion	X					
Photovoltaic						
Residential/Commercial	X					
Ground Central Station	X					
Space Central Station	X					
Wind Energy Conversion	X	X	X			
Ocean Thermal Difference	X	X	X			

X indicates effort is under way but not necessarily complete.

capital cost reductions are the major problems standing in the
way of large-scale application of thermal conversion and photo-
voltaic systems, and low-cost materials and materials processing
methods are principal factors in achieving this goal. For this
reason the ARPA Materials Research Council can make a valuable
contribution in both identifying the important materials
problems that will pace the orderly development of these tech-
nologies and generating innovative approaches toward their
solution.

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SOLAR ENERGY APPLICATIONS

Michael B. Bever

Abstract

This memorandum is concerned with applications of solar energy to thermal energy utilization, electric power generation and the promotion of chemical, biochemical and biological processes.

In Part I current applications such as water heating, distillation, drying of products, sewage treatment, solar furnaces and electric power for space vehicles are described. Installations in the experimental stage such as space heating and cooling and in situ power generation are discussed. Schemes proposed for future development such as large-scale power generation and the production of synthetic fuels by solar energy are considered.

Part II deals with common characteristics of solar energy applications and draws some conclusions. Part III is a bibliography of solar energy applications.

SOLAR ENERGY APPLICATIONS

Michael B. Bever

This memorandum is concerned with applications of solar energy. Part I surveys past and current applications and proposals for future development. Part II deals with common characteristics of solar energy applications and draws some conclusions. Part III is a bibliography of solar energy applications.

Part I. Survey of Solar Energy Applications

Solar energy applications may be divided into four major groups:

(1) thermal

(2) direct electrical

(3) chemical, biochemical and biological, and

(4) indirect applications.

Table 1 shows a classification scheme based on these groups.

In the first part of this memorandum we shall describe the applications. We shall indicate their current status, which ranges from commercial readiness to merely speculative schemes. Assignment of status is a matter of judgment; moreover, the status of some proposed applications may change rapidly.

1. Thermal Applications

The direct thermal applications of solar energy can be subdivided according to the temperature ranges of the utilized heat. The low-temperature

range extends from room temperature to 100°C, the medium- and high-temperature range from 100°C to over 1,000°C and the ultra-high temperature range upward to 3,500°C.

The technical feasibility of the low-temperature heat applications of solar energy listed under 1.1 in Table 1 has been established and several of these applications are in current use. In cool climates direct solar heating of space by appropriate exposures has always been practiced. Buildings which have facilities for collecting and storing heat have been constructed for experimentation and demonstration. Also a few installations of space cooling or refrigeration have been reported. Combined heating and cooling systems for private residences as well as commercial and industrial buildings are of special interest. Solar water heating for residential and institutional use is established practice in several countries.

Industrial utilization of low-temperature solar heat includes some ancient techniques such as the production of salt by evaporation of sea water and the drying of agricultural products. Solar drying is not necessarily limited to low-temperature heat and could be applied to industrial products. Solar drying of oil shale has special interest at present.

Brackish water has been distilled for domestic and agricultural purposes in isolated locations or small municipalities in Australia, the West Indies and elsewhere. Large-scale desalination based on solar energy has been proposed but the projected costs make it economically unattractive for the foreseeable future.

Solar energy has been successfully applied to sewage treatment as a source of heat for the digesters; it seems to deserve wider adoption. The stimulation of plant growth in greenhouses is a long established

utilization of low-temperature solar heat; in a more sophisticated form
it could probably be applied to vegetable growing in arctic climates.

The feasibility of several applications of medium- and high-
temperature solar heat has been demonstrated. Technically satisfactory
equipment for cooking and baking is available but apparently has not been
adopted by those population groups in developing countries for whom it
was intended and who spend an appreciable fraction of their cash income
on fuel for food preparation. Hot-air engines and steam engines using
solar thermal energy have been successfully demonstrated. They seem to have
particular merit for irrigation pumping but have not been adopted on a
significant scale. Steam produced by solar energy could also serve as the
basis of solar thermal power stations.

Solar energy is singularly well suited for the generation of ultra-
high temperature heat. The heat can be directly beamed onto a metallur-
gical or chemical charge instead of having to be transmitted through a con-
taining vessel with the attendant risk of contamination. Solar furnaces
employ such ultra-high temperature solar heating. Solar furnaces are
being developed on a sustained basis in the French Pyrenees. An experi-
mental solar furnace was in operation in Southern California in 1950. A
solar furnace for research in thermal shock is a unique example of high-
temperature solar heating. Solar furnaces are technically successful,
but the prospects for their industrial acceptance appear uncertain.
Even for experimental work, the imaged arc electric furnace seems to be a
more convenient technique of ultra-high temperature heating.

In summary, the utilization of direct thermal solar heat has been
successfully demonstrated for the low-temperature, medium- and high-temperature

-64-

and ultra-high temperature regions, but only low-temperature applications have so far been adopted for large-scale routine use. Also, the prospects of a rapid expansion of solar thermal energy utilization appear to be most promising for this temperature range. The contributions of low-temperature solar heat should not be underestimated. Since in this temperature range the alternative heat sources such as oil or electricity are utilized in the most wasteful manner, solar energy is particularly effective from the standpoint of over-all energy conservation.

2. Direct Electrical Energy

Electrical energy can be produced by direct conversion of solar energy without a mechanical intermediary. The direct conversion can be carried out by the photovoltaic, thermoelectric, and galvanovoltaic effects.

The photovoltaic effect has been used on a small scale in space vehicles. This application has demanded great reliability and high efficiency, but there were essentially no economic restraints. The successful space application of photovoltaic electricity generation has been important in focusing attention on solar energy utilization but has also given rise to misunderstandings of the technical and economic limitations of photovoltaic conversion technology.

Small-scale, ground-based applications of the photovoltaic effect have been made on a limited scale particularly for the continuous charging of batteries ("solar batteries"). These devices are attractive for communication and navigation equipment in inaccessible locations. Operating problems which may have arisen (for example, through the actions of animals or birds) presumably can be overcome. Some small-scale, ground-based

applications of the photovoltaic effect have potential military interest.

The use of photovoltaic cells for in situ generation of electricity in buildings has reached the pilot stage. Electricity generated in this manner is available for a variety of functions including heating and cooling in conjunction with a heat pump. Such installations will require stand-by public-utility power or large storage capacity.

The large-scale ground-based use of the photovoltaic effect is envisaged in the concept of "solar farms" proposed for sunny, arid regions in the Southwestern United States. Another proposed large-scale application of the photovoltaic effect involves a space-based satellite for the collection of solar energy and its conversion to electricity which is to be beamed to a terrestrial receiving station. Its obvious advantages include operation essentially independent of weather and seasons and limited interference with the environment; the complexities and costs of such a scheme are equally obvious.

The thermoelectric effect attracted attention in the 1940's and 1950's as a possible means of producing electric power from solar energy. Low efficiencies and high costs, however, have discouraged this approach. The galvanovoltaic effect, which is another possibility, also presents great technical challenges. This method is considered elsewhere in this Report.

A combined approach to obtaining thermal and direct electrical energy from solar energy approaches the "total energy concept" and has special attractions. Such a combination would be of particular interest for use in buildings and for remote locations.

3.   Chemical, Biochemical and Biological Applications of Solar Energy
       Solar energy has great potential for promoting chemical and

biochemical reactions and biological processes for the production of fuels. A great deal of research and development, however, will be necessary before practical engineering methods will be available.

The dissociation of steam has been suggested as a promising reaction for the chemical conversion of solar energy. Since this would require high temperatures, it could benefit from available solar furnace technology.

The technology of biochemical and biological energy conversion processes has attracted little attention to date. Naturally occurring photosynthesis can serve as one base for further studies. The biogeneration of fuels, such as hydrogen or methane, is attractive, but workable processes for operation on an adequate scale are still lacking.

4.   Indirect Applications of Solar Energy

Several indirect applications of solar energy are mentioned here for completeness. They include the exploitation of hydroelectric power, wind power, and ocean thermal gradients.

Part II.   Characteristics and Problems of Solar Energy Applications

1.   General Features

The applications of solar energy described in Part I have certain general features in common. Each application involves collection, conversion and storage but one or two of these functions may be undeveloped. For example, the utilization of solar energy as low-temperature thermal energy requires no special equipment for conversion; the resulting

simplicity and economy of operation is one reason why this mode of solar energy utilization has been most widely adopted.

The intermittent nature of solar energy requires energy storage; otherwise, its application would be severely limited. Solar heating installations are equipped with heat reservoirs; the cost of the equipment for heat storage is a large part of the cost of such installations.

The direct in situ generation of electrical energy requires storage batteries in addition to a conversion device. The proposed schemes for large-scale generation of electricity provide for storage by the production of a synthetic fuel or other intermediate product.

2.   Scale and Location of Solar Energy Applications

Solar energy can be converted into usable form at the point of consumption as thermal or electrical energy. Solar space and water heating and space cooling are decentralized by their nature. In situ generation of electricity is also possible and eliminates transmission losses and the need for transmission facilities. The question arises as to what extent distribution systems of the public utility type can ultimately be dispensed with or whether electric power from solar energy will be generated in central stations. Any system producing synthetic fuels from solar energy would necessarily be centralized.

The in situ generation of electricity for consumer use probably will involve photovoltaic conversion. Without adequate and reliable storage of electric energy, however, public utility power on a standby basis would still be required and is provided for in current pilot installations.

The degree to which any type of solar energy application can be

dispersed depends on the degree of its technical complexity: the least complex can be the most dispersed. Space and water heating and space cooling are favored in this regard.

Solar energy has its greatest potential in the "sun belt" which includes the Mediterranean countries, certain parts of Africa, Southern Asia, Australia, the Carribean, and parts of South America. Large sections of these regions are underdeveloped and lack energy resources. Solar energy applications, therefore, should be of particular interest to them and in fact the largest fraction of operating installations are located there. A continuation of this trend is also of broad international importance since it will limit new demands on the global supply of fossil fuels which is already being strained by the older industrialized regions.

Solar energy can also make major contributions in the temperate zone. Climate appears to be more important than geographical latitude. Various parts of the United States are potentially suitable sites for intensive solar energy applications and limited applications are possible almost anywhere in this country.

3.   Sequence of Future Development

The sequence of significant impacts of solar energy applications is likely to be in the order of private residences, office and institutional buildings, military installations, agriculture and industry, and public utilities.

Military installations allow experimentation with solar heating and cooling of multiple units under controlled conditions. They also provide opportunities for applying the total energy concept, perhaps in combination with nuclear energy. This would be of particular interest in remote sites

-69-

where combined solar and nuclear power sources could reduce logistic problems. The application of solar energy to the distillation of brackish water and sewage treatment for military installations should also be considered.

The application of solar energy to sewage treatment and to water distillation in isolated locations is of general interest. Agricultural and industrial applications, especially to the drying of materials, including mineral materials, warrant intensified development efforts.

4.   Environmental Aspects

Solar energy applications make few undesirable impacts on the environment. They do not generate products of combustion nor do they cause any other atmospheric or water pollution. Most solar energy applications create no thermal pollution on the global scale since their effects on the over-all terrestrial heat balance cancel. Effects on local heat distribution are minor except for solar farms which also raise questions concerning land use.

The utilization of solar energy for residential purposes has created some architectural problems. The equipment is bulky and adds unaccustomed features to the appearance of residential structures. Solar water heating installations reportedly have met with aesthetic objections. Solar equipment for cooking and baking was a technical but not a practical success, probably for psychological or sociological reasons. It seems that aesthetic and psychological objections can be overcome.

5.   Energy Conservation

The obvious driving force for the development of solar energy is its potential contribution to energy supplies. The NASA-NSF study, for

example, expressed confidence that "solar energy can meet a sizable portion of the nation's future energy needs" - perhaps as much as one-third of the total heating needs. A report to the Federal Power Commission estimates that by the year 2020 solar energy will contribute a minimum of 7.6 percent and a maximum of 26 percent to the total energy supply in this country. The necessary retrofitting of existing structures is a major obstacle to the expansion of residential uses. This problem has not attracted as much attention as it deserves.

The most immediate applications of solar energy will be in low-temperature thermal energy utilization. This is of particular benefit because solar energy used for these low-grade energy needs would replace high-grade energy fossil fuels. The substitution of solar energy for imported oil will improve the balance of payments of the United States.

6.   Economic Aspects of Solar Energy Applications

Solar energy applications are capital-intensive, because most of them require expensive equipment. This will retard their adoption. Especially in the case of residential applications, high equipment costs will tend to discourage prospective homeowners. Special financing of such installations in private housing should be provided.

Solar energy applications generally do not present opportunities for economics of scale either in construction or operation. Most costs are a linear function of capacity.

Since the energy input in solar energy applications is "free", efficiency is mainly important because of the cost of the equipment. In space and some military applications, weight and volume efficiencies also

count. In these applications higher costs for the sake of reliability are more acceptable than for civilian uses.

The costs of collection of solar energy have been estimated to range from 50 to 95 percent of total costs. Storage costs may be as high as 25 percent.

In order to be competitive, solar energy must compete in over-all costs with comparable fuel-operated devices - in other words, it must be cheaper. This points up the importance of comparative fuel prices. Comparisons published very recently, however, are now out of date because of the new level of oil prices. For example, the standing of solar space heating relative to oil heating has become less unfavorable than their respective positions in Figure 4 of the NASA-NSF study.

7.   Materials Problems

The materials problems of solar energy applications are those of the collection, conversion and storage subsystems. They involve performance and efficiency, cost and minimum life expectancy.

The collection function in dispersed, small-scale installations for low-temperature thermal energy presents no major materials problems. The proposed large-scale projects, especially if they employ focussed radiation collection, will require large amounts of transparent materials. Their cost is an appreciable item. Large-scale collection facilities would also raise serious questions concerning the durability and degradation resistance, particularly of plastics and glass, in exposure to intensive solar radiation. Little technical experience seems to exist regarding degradation resistance, long-term dimensional stability, and heat shock resistance of materials under these circumstances.

Energy conversion by photovoltaic cells or other devices depends on special physical properties. These properties are discussed in other memoranda in this Report. The conversion materials present major production problems, including their cost of production; also, there are questions concerning their life expectancy.

Energy storage poses materials problems. For example, the storage of low-temperature thermal energy for space heating still presents a technical and economic challenge. Some materials problems of energy storage are discussed in Volume I of this Report.

Part III. <u>Bibliography</u>

See next page.

Acknowledgement

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Table 1. Applications of Solar Energy

1. Thermal

1.1 Low-temperature heat

1.1.1 Water heating
1.1.2 Space heating
1.1.3 Space cooling and refrigeration
1.1.4 Combined heating and cooling
1.1.5 Salt production
1.1.6 Drying of agricultural products,
mineral products, industrial products
1.1.7 Distillation - desalination
1.1.8 Sewage treatment
1.1.9 Stimulation of plant growth

1.2 Medium- and high-temperature heat

1.2.1 Cooking, baking
1.2.2 Hot air engines
1.2.3 Steam for mechanical power
1.2.4 Steam for electrical power

1.3 Ultra-high temperature heat

1.3.1 Solar furnaces

2. Direct Electric Applications

2.1 Photovoltaic cell

2.1.1 Small-scale, space-based
2.1.2 Small-scale, ground based:
"solar battery", power package
2.1.3 Large-scale, ground based:
"solar farm"
2.1.4 Large-scale, space-based

3. Chemical, Biochemical and Biological Applications

3.1 Chemical conversion

3.1.1 Dissociation of steam

3.2 Biochemical and biological

3.2.1 Photosynthesis
3.2.2 Biogeneration of fuels

-79-

4. Indirect Applications

    4.1 Hydroelectric power
    4.2 Wind power
    4.3 Ocean thermal gradients

COMMENTS ON DISCUSSION OF SOLAR ENERGY CONVERSION

J. J. Gilman

1. The analysis of realistic and complete systems is receiving too little attention. The analysis that is being done (and published) is the work of proponents of particular conversion systems. These analyses are often incomplete.

Total capital costs are being underestimated as are operating costs such as maintenance and storage. Present values (cash flow analyses) for various projects are not commonly computed for comparison with other options.

Cost reductions are being anticipated for components based on past experience. In a rapidly changing world economic structure, this method is not a realistic basis for justifying spending budgets at rates as high as tens of millions of dollars per year. In some cases the present "applications" work is based on subsystems that are known to be inadequate because of poor performance or high cost.

2. Since incoming terrestial solar power is intermittent and often aperiodic it is clear that sophisticated storage systems are crucial to any substantial solar energy system. Also, such systems will make major contributions to overall system capital and maintenance costs. Far too little attention is being given to them. In fact, my analysis of the FY73 - NSF Budget indicates

-81-

that zero attention is being paid by this organization. If an economically and technically adequate storage system is not available there is little point in developing large scale collecting systems.

3. More research attention should be given to photochemical conversion techniques because they are relatively unexplored and therefore have the greatest potential for novel discoveries as a result of exploration. These techniques include:

a. bio-conversion - use of algae-bacterial systems to perform the overall reaction:

$$2H_2O + CO_2 \xrightarrow{h\nu} CH_4 + 2O_2$$
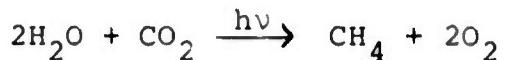
b. photogalvanic action at membranes - this is the ionic analog of the electronic photovoltaic cell.

c. photo-assisted electrolysis of water or other substances to produce fuels.

d. photo-activated adsorption for separations of mixtures of phases.

e. artificial photosynthesis of hydrocarbons.

f. photo-activated catalysis.

g. long-lived excitonic storage of photons for activating selected chemical reactions.

h. resonant two photon up converters for skewing solar frequency distribution toward higher frequencies.

i. phosphors for concentrating broad-band incident

radiation into a desirable narrow band.

j.   photo-activated permeation through membranes.

THERMAL INSULATION OF WINDOW GLASS

A. J. Sievers

Abstract

The thermal insulation of window glass is increased
by a factor of two with a simple spray-on conductive coating.

THERMAL INSULATION OF WINDOW GLASS

A. J. Sievers

A traditional style dwelling with about 10% of its
wall area devoted to single pane windows loses from 30 to 50%
of its heat energy through these windows. With properly fitted
storm windows the heat loss is reduced to about 10 to 15% of
the total. Double glazing (two panes of glass separated by a
small air space and mounted in the same frame) would reduce the
heat loss to the 15 to 25% range but as a modern style house
has almost twice the window area of a traditional house the
percentage heat loss remains quite large. Infrared radiation
plays a major role in accounting for these losses. We show that
a commercial spray-on conductive coating, SnO_2,[1] which is trans-
parent in the visible decreases the infrared emissivity of glass.
This lower emissivity significantly decreases the heat loss
through single panes, double glazed and storm windows. For
special coatings of SnO_2:Sb [2] or In_2O_3:Sn [3], which are not yet
commercially available, the heat transmission is decreased by
at least a factor of two for all three window geometries.

The power radiated by a body depends on its temperature
and its emissivity as given by the Stefan-Boltzmann law

$$W = \varepsilon\sigma T^4$$

where ε is the emissivity of the surface and varies from 0 for a perfect reflector to 1 for a perfect absorber (black body). In Eq. 1, $\sigma = 0.17\times10^{-8} \dfrac{BTU}{ft^2 hr(°R)^4} = 5.67\times10^{-8} \dfrac{watt}{m^2 (°K)^4}$.

The spectral distribution of the radiation is given by the Planck radiation law. For our purposes it is sufficient to identify a few characteristic wavelengths associated with the distribution.

Only two percent of the energy is found below a wavelength, λ_{min}, given by

$$\lambda_{min} T = 1600 \text{ micron } °K,$$

fifty percent of the energy is found below a wavelength, $\lambda_{\frac{1}{2}}$, given by

$$\lambda_{\frac{1}{2}} T = 4100 \text{ micron } °K$$

and ninety-eight percent of the energy is found below a wavelength λ_{max} given by

$$\lambda_{max} T = 18000 \text{ micron } °K$$

For a room temperature radiator these three wavelengths are the value of the emissivity in the far infrared region of the electromagnetic spectrum between

$$\lambda_{min} = 5.3 \text{ micron}$$
and

$$\lambda_{max} = 60 \text{ micron}$$

determines the radiated power.

To estimate the relative importance of heat transport by radiation we calculate the net radiative transfer of heat between two glass surfaces separated by a small air space and compare it to the conductive transport. The small spacing insures that convective heat transport is suppressed.

Area A_1 of emissivity and absorptivity ε_1 at T_1 is opposite area $A_2 = A_1$ of emissivity and absorptivity ε_2 at T_2. In unit time, unit area of plane 1 emits $\varepsilon_1 \sigma T_1^4$ of which the fraction ε_2 is absorbed and $(1-\varepsilon_2)\varepsilon_1$ is reflected back towards A_1 and partially absorbed etc. The resulting infinite geometric series expressing absorption at A_2 is

$$W_{1 \rightarrow 2} = A_1 \sigma T_1^4 \; \frac{1}{\dfrac{1}{\varepsilon_1} + \dfrac{1}{\varepsilon_2} - 1}$$

The absorption at A_1 can be obtained by interchanging the indices so the net radiative transfer with $A_1 = A_2 = A$ is[4]

$$W_{Net} = \frac{A\sigma}{\left(\dfrac{1}{\varepsilon_1} + \dfrac{1}{\varepsilon_2} - 1\right)} \; (T_1^4 - T_2^4)$$

or for small temperature differences the power transmitted per unit area per degree temperature difference is

$$R = \frac{W_{net}}{A \; \Delta t} = \frac{4\sigma T_1^3}{\dfrac{1}{\varepsilon_1} + \dfrac{1}{\varepsilon_2} - 1}$$

In the infrared between 5 and 60 micron wavelength glass has a ery large absorptivity so we set $\varepsilon_1 = \varepsilon_2 = 1$.

$$R = 6.1 \ (\frac{\text{Watts}}{\text{m}^2 \ °\text{C}}) = 1.1 \ (\frac{\text{BTU}}{\text{hr f}^2 \ °\text{F}})$$

With the two panes of glass separated by ∿1", convection is suppressed and the heat transmission due to conduction alone is

$$C = 0.9 \ \frac{\text{Watts}}{\text{m}^2 \ °\text{C}}$$

so

$$\frac{R}{C} \simeq 6.5 \quad .$$

Even at room temperature radiation is the dominant heat transfer mechanism. Consequently, the emissivity of glass in the infrared plays a major role in the thermal insulation of windows.

Tin oxide in the form of a thin film on glass has been used for a number of years as a transparent electrode or as a transparent heater. These films are usually applied by spraying a mixture of $SnCl_4$ with ethanol onto a glass substrate which has been heated to 400°C. The $SnCl_4$ is transformed into semiconducting SnO_2.

In the wavelength region from 5 to 30 microns the SnO_2 coating is observed to reduce the infrared emissivity of window glass by about 10%.[5] This change is associated with the free carriers in the semiconducting SnO_2. As the carrier concentration is small the plasma frequency ($\omega_p = \sqrt{\frac{4\pi Ne^2}{\varepsilon_o m}}$) associated

-89-

with the free carriers occurs below the frequency region of interest. Recently, carrier concentrations $N \simeq 10^{20}$ cm^{-3} have been achieved by adding some SbCl$_3$ or HF to the SnCl$_4$ solution before spraying.[6] In this case the plasma resonance occurs at smaller wavelengths ($\simeq 2\mu$) and the emissivity is reduced to $\varepsilon = 0.2$ between 5 and 60 microns. An even smaller emissivity, $\varepsilon = 0.1$, has been observed for In$_2$O$_3$:Sn [3] in this wavelength region.

We have estimated the power transmitted per unit area per degree temperature for a single pane of glass, for double glazed glass ($\frac{1}{4}$" spacing) and for storm windows (1" spacing). These results are summarized in Table 1. An $\varepsilon = 0.9$ is assumed for the uncoated glass and an $\varepsilon = 0.1$ for the coated glass. Natural convection plus radiation heat transfer is taken into account for the two exposed glass surfaces. In all three cases we have assumed that the temperature difference between the air and the glass is less than 20°F.

From the literature the coefficient for heat transmittance in $\frac{BTU}{hr\ f^2\ °F}$ (U-no.) for a single glass pane is $U = 1.1$ and for a storm window $U = 0.5$.[7] The corresponding calculated values in Table 1 for $\varepsilon = 0.9$ compare reasonably well with these experimental U-nos.

It is evident from the $\varepsilon = 0.1$ column of Table 1 that a factor of two decrease in heat transmission can be expected for all three geometries. It should also be mentioned that

these coatings actually toughen the glass surface. Because of
the incipient national fuel shortage, glass companies sould be
encouraged to mass produce coated glass for home construction.

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TABLE 1.   Power Transmitted $\left(\dfrac{W}{m^2 \ ^\circ C}\right)$ For Different

Window Geometries.   (The corresponding U-nos.

in $\dfrac{BTU}{f^2 \ hr \ ^\circ F}$ are given in parentheses.)

	$\varepsilon = 0.9$	$\varepsilon = 0.1$
Single Pane	≥ 8 (1.4)	≥ 4 (0.7)
Double Glazed ($\frac{1}{4}$" spacing)	4.4 (0.8)	2.2 (0.4)
Storm Window (1" spacing)	3.8 (0.67)	1.5 (0.27)

AN ALTERNATIVE TO FLAT AREA
SOLAR ENERGY ABSORPTION UNIT DEPLOYMENT

J. P. Hirth

Flat area deployment of solar energy absorbers has some possible disadvantages which would be overcome by vertical disposition in a building. These include (1) increasing usage of land area, (2) complete shadowing of the underlying land area with possible adverse environmental effects, and (3) where storage is important, long distance transmission to a storage device or, with say rooftop disposal, numerous individual storage units.
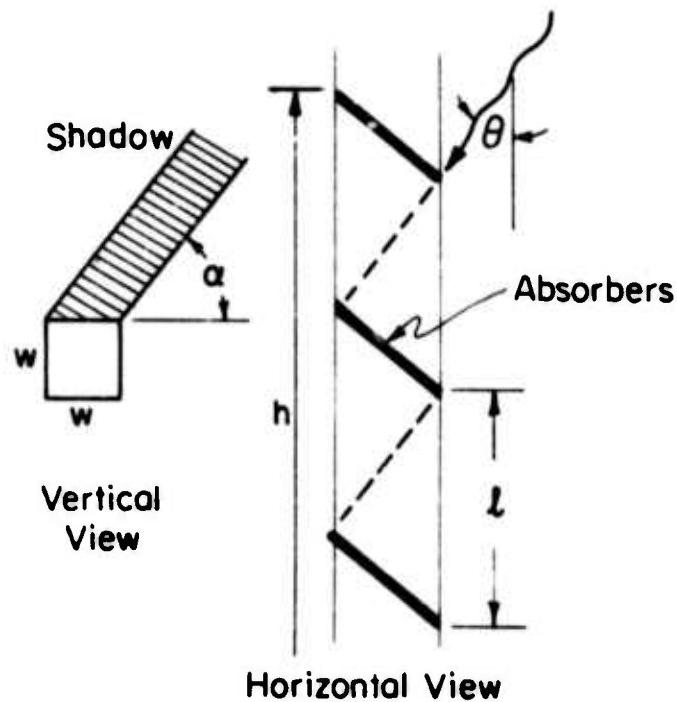

Figure 1. Vertical Array

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With the vertical array, the total area exposed to the sun is

$$A = hw \sin \theta \qquad\qquad (1)$$

Here, h is the total height of the array and θ is the angle between the incident rays from the sun and the normal to the earth's surface. Evidently the area A in equation (1) can exceed w^2 provided θ is nonzero, which it never is in the U.S., so more area of exposure can be achieved per unit area w^2. An even greater area of exposure per base area w^2 would be achieved by using lateral extension panels. Moreover, the shadow rotates through an angle α of the order of 150° during a day so that any given area in the vicinity is shadowed only a fraction of the time. Finally, a central storage unit could be used at the site, reducing the above problems with numbers of units or distance of transmission. A possible disadvantage would be the cost of the structure, but this would have to be traded off with the above possible advantages.

Acknowledgement

OPTICAL ANALYSIS OF SOLAR-THERMAL
ENERGY COLLECTION

P. L. Richards

Abstract

A brief analysis is presented which illustrates how
design parameters such as the concentration factor and the
operating temperature interact with the optical parameters
of materials in the system design of thermal solar energy
collectors. The use of wedge concentrators is suggested as
an economical way to achieve large concentration factors.
A schematic system design is given to illustrate the use of
such concentrators.

OPTICAL ANALYSIS OF SOLAR-THERMAL ENERGY COLLECTION

P. L. Richards

I. Introduction

Thermal schemes for harvesting solar energy generally
involve a collecting surface such as a mirror or a lense with
area A_s which focuses the sunlight onto a heat exchanger with
absorbing area A_p and absorptivity α_p (averaged over the solar
spectrum). The ratio of these two areas $A_s/A_p = K$ can be called
the concentration factor. The product $A\Omega$ of the area of an
illuminated surface times the solid angle subtended by the
source at that surface is an invariant quantity called the
throughput of an optical system. The smallest possible absorber
area $A_p = A_s\Omega_s/\Omega_p$ occurs when the sunlight is focused onto the
absorber from all angles, $\Omega_p = 2\pi$. The sun subtends a solid
angle $\Omega_s \simeq 6 \times 10^{-5}$ sterad when viewed from the earth, so the
ideal concentration factor $K_{max} = 2\pi/\Omega_s \simeq 10^5$. With such an
optimum optical system an absorber, which is otherwise thermally
isolated, would reach radiation equilibrium at the effective
solar temperature $T_s \simeq 5,000K$.

In a power collection system, the balance between the
solar power input, the various heat losses, and the useful
energy carried away by the working fluid will be such as to

maintain the heat exchanger at a convenient operating temperature T_p. For a steam turbine power generation system this temperature would be $T_p \simeq 500°C = 773K$.

One source of heat loss in such a system is the power radiated from the absorbing surface, $P = \epsilon_p A_p \sigma T_p^4$, where ϵ_p is the emissivity of the surface averaged over the (infrared) black body spectrum emitted at temperature T_p and σ is the Stefan-Boltzmann constant. For a system with the ideal concentration factor defined above, the fraction of the incident solar power which is lost by re-radiation is $\left(\frac{T_p}{T_s}\right)^4 \frac{\epsilon_p}{\alpha_p} \simeq 6 \times 10^{-4} \, \epsilon_p/\alpha_p$. Clearly this heat loss is negligible for any reasonable values of the quantity α_p/ϵ_p.

In any practical system the achievable concentration K will be less than K_{max}. Even when constructed with expensive optical components, most systems cannot concentrate the solar radiation into a 2π solid angle. The heat absorbing surface, however, will still radiate into a 2π solid angle. Because of the conservation of thruput, the fraction of the power radiated away is increased by the factor K_{max}/K.

The concentration factor can also be reduced by aberrations in inexpensive imaging systems. It may therefore be necessary to make A_p much larger than the theoretical minimum in order to intercept an acceptable fraction of the solar energy with inexpensive structures. The fraction x of the incident solar energy which is lost by re-radiation for a system with a given α_p/ϵ_p and concentration factor is

$$x = \frac{K_{max}}{K} \frac{\varepsilon_p}{\alpha_p} \left(\frac{T_p}{T_s}\right)^4 \simeq \left(\frac{\varepsilon_p}{\alpha_p}\right) \quad .$$

In the literature of solar energy collection, systems with $K \simeq 60$ are referred to as "high concentration" systems. For $K \lesssim 60$ the quantity α_p/ε_p is an important parameter.

In order to harvest diffuse as well as direct sunlight, non-concentrating systems with $K = 1$ are required. For such systems α_p/ε_p must be of the order of 60 for $T_p = 500°C$ if the extra energy from the diffuse sunlight is not be radiated away. This very stringent condition is rapidly relaxed if the operating temperature T_p is allowed to drop below 500°C. Values of $\alpha_p/\varepsilon_p \simeq 5$ are generally available from simple stable compounds[1], while values up to 20 have been produced with sophisticated multi-layer coatings[2].

II.   Structures which Optimize Solid Angle

As was discussed above, the concentration factor of a given system is improved if the sun is imaged on the absorbing surface with a solid angle approaching 2π. Most fast mirror or lense systems require accurate curved surfaces which are usually expensive to fabricate. The cone (in three dimensions) or wedge concentrator (in two dimensions) offers an alternative approach which may have economic advantages. The analysis of such cones has been given by Williamson[3], and their use with solar cells has been discussed by Ralph[4]. The geometrical construction given in Fig. 1 shows that the area of an absorbing surface

placed at the small end of the cone is effectively increased
for rays entering the large end of the cone. Consequently,
solar radiation which is incident with solid angle Ω_p on an
absorber of area A_p without a cone, can be concentrated into a
smaller area approaching $A_p \Omega_p / 2\pi$. The maximum concentration
factor is obtained for a long cone with a field lense and high
reflectivity surfaces. Economic factors will probably favor the
use of relatively short simple cones which improve the concen-
tration by a factor of 3-5.

III.   Structures which Minimize Radiation Loss

We have seen that for systems with a small concentration
factor a large α_p / ε_p is required to avoid excessive radiation
loss. The extreme thermal environment and the long life required
for a practical system complicates the use of sophisticated multi-
layer coatings with high α_p / ε_p on the absorbing surface. The
value of α_p / ε_p obtainable in practice will probably be limited
by material lifetime problems. The possibility exists of using
various structures around the absorbing surface to modify its
performance so that the radiation heat loss is relatively in-
sensitive to the properties of the absorber used. A simple
collector surface material with moderate α_p / ε_p, designed to
withstand temperature extremes, can have its performance enhanced
by a more sophisticated coating on a heat mirror which is main-
tained near ambient temperature.

The idea is illustrated in Fig. 2 where we show a heat exchanger pipe with area A_p whose surface is characterized by α_p/ε_p which is partially surrounded by a reflecting pipe whose inner surface is characterized by A_R and ε_R. A gap in the reflecting pipe is covered by a mirror of area A_m characterized by a high average transmittance T_m for solar radiation and a high reflectivity R_m for re-radiated infrared. This center pipe should be sealed and evacuated to prevent convective heat loss from the heat exchanger.

A heat mirror with $R_m \simeq 0.9$ and $T_m \simeq 0.8$ can be constructed from Sn doped In_2O_3 deposited on glass[5]. The inner reflecting surface of the vacuum jacket could be aluminized to give $\varepsilon_R \leq 0.05$. All of these coatings would operate near ambient temperature in a vacuum environment, so should have long life.

The distribution of infrared photons between the pipes is essentially uniform because all surfaces have at least moderately high reflectivities. The power radiated from the heat exchanger pipe is $P = \sigma T_p^4 \varepsilon_p A_p$. If we neglect infrared radiation from objects at ambient temperature, which is reduced by the factor $(T_A/T_p)^4 \simeq .02$, the power lost from the heat exchanger can be written

$$P_L = \frac{\sigma T_p^4 \varepsilon_p A_p [\varepsilon_r A_r + (1-R_m)A_m]}{\varepsilon_r A_r + (1-R_m)A_m + \varepsilon_p A_p}$$

Several limiting cases can be explored in order to illustrate the usefulness of this uniform photon density analysis.

1. Consider first the limit of a large mirror area with no coating. In this case $A_m \gtrsim A_p$, and $R_m = 0$ so that $(1-R_m)A_m$ dominates both numerator and denominator. Then $P_L = \sigma T_p^4 \epsilon_p A_p$ so that all of the power radiated from the heat exchanger is lost.

2. Now consider the case of a small mirror area without a coating, $A_m \ll A_r \simeq A_p$ and $R_m = 0$. We then have $\epsilon_p A_p$ much larger than A_m or $\epsilon_r A_r$ so that $P_L = \sigma T_p^4 A_m$. A small hole in the outer pipe thus acts like a black body radiator at temperature T_p.

3. The cases of greatest interest are those with an efficient heat mirror $R_m \gtrsim 0.9$. First assume that all areas are comparable $A_m \simeq A_p \simeq A_r$ and that $\epsilon_r \lesssim 0.05$. Then $\epsilon_r A_r$ can be neglected and $P_L \simeq T_p^4 \epsilon_p A_p (1-R_m)/[(1-R_m) + \epsilon_p]$. Clearly, the power lost is determined by either $\epsilon_p A_p$ or by $(1-R_m)A_m$, whichever is smaller. A high performance heat mirror operating at ambient temperature can be used in place of a low emissivity coating on the hot heat exchanger.

4. A heat mirror can also be used in non-concentrating systems with $A_r = 0$ so that sunlight can reach the heat exchanger from all directions. If we continue to assume that $A_m \simeq A_p$ then the expression for P_L is the same as for case 3 above. The power lost again depends on the smaller of $(1-R_m)$ or ϵ_p.

An analogous analysis can sometimes be useful in understanding the absorption of solar energy. The heat mirror reduces the incident power by T_m whenever it is used. A reflecting surface surrounding the absorber, as is the case for example 2 above, converts the system into a black body absorber with effective area A_m for a wide range of values of α_p. The assumption of uniform distribution of photons made in this analysis permits only qualitative conclusions for cases 1 and 2 above, but should yield accurate results for cases 3 and 4.

IV.   System Optimization

The analysis discussed above is intended to display the interrelationship between various material properties and system performance. A thorough engineering analysis based on available, or developable material properties and on material and fabrication costs would be required to obtain an optimum system design for a specific location. Such a study is beyond the scope of this paper.

In the absence of an engineering analysis it is interesting to speculate on the general form which an optimized system might take. Figure 3 contains a suggested heat exchanger structure for a high concentration system of the type which might prove useful in locations which have a large proportion of direct sunlight. The entire structure is kept small relative to the collector for low cost and is evacuated to avoid convection losses. The heat exchanger pipe is partially surrounded

with radiation shields such as thermally isolated sheets of shiny aluminum foil. Because they reach radiation equilibrium at intermediate temperatures, each sheet with (low) emissivity ε_s reduces the radiative heat loss from the back of the pipe by a factor $2/\varepsilon_s$. The absorbing sector of the pipe is coated with material with the highest available α_p/ε_p consistent with long life and low cost. Because a heat mirror is used, it may be more important to increase α_p than to reduce ε_p. A wedge concentrator of shiny aluminum foil or aluminized glass is used to concentrate the solar energy. A heat mirror is deposited on the inner surface of the glass pipe. The heat mirror should be far from the absorbing surface because suitable coatings have larger T_s near normal incidence. This factor may not be of primary importance, since R_m will increase for infrared rays far from normal incidence. The separation of the mirror from the absorber determines the diameter of the glass vacuum pipe, which is drawn with a circular cross section for ease of fabrication. If this pipe is kept small for low cost, it may prove desirable to extend the wedge concentrator outside the pipe as shown.

Acknowledgement

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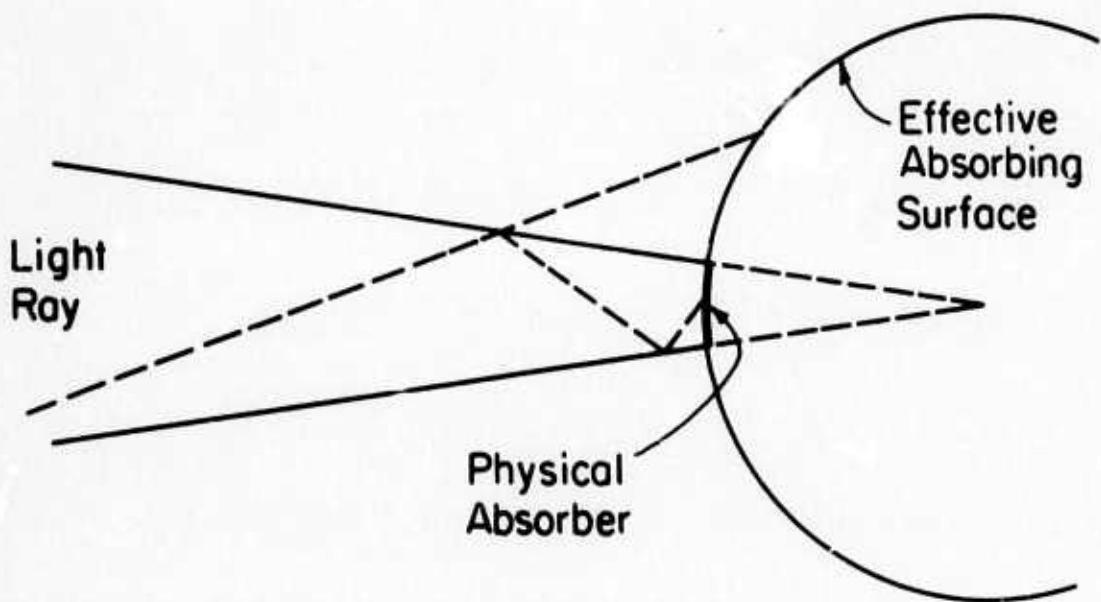
Figure 1.   Illustration of the optical properties of a cone
            or wedge concentrator. The angle of incidence
            of the light ray on the effective absorbing surface
            is the same as the angle of incidence of the re-
   flected ray on the physical absorber.
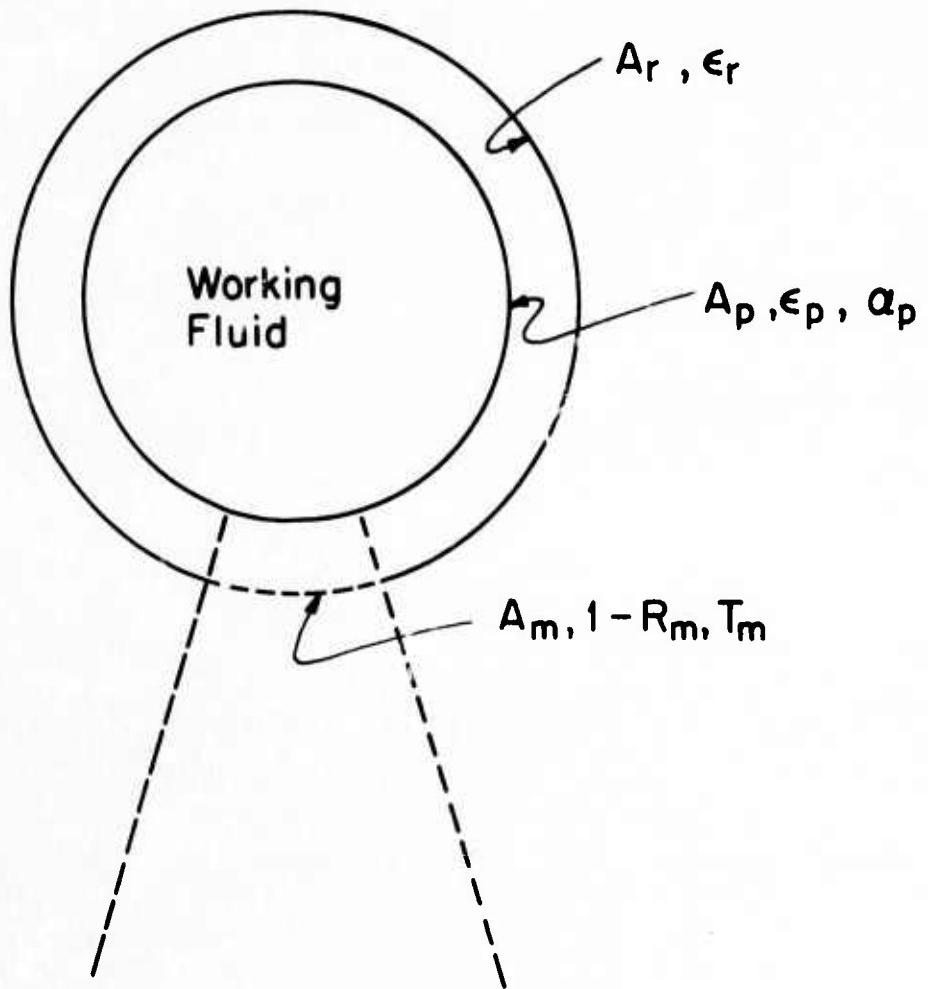
Figure 2. Illustration of a heat exchanger pipe of area A_p partially surrounded by a reflecting surface of area A_r and partly by a heat mirror of area A_m.
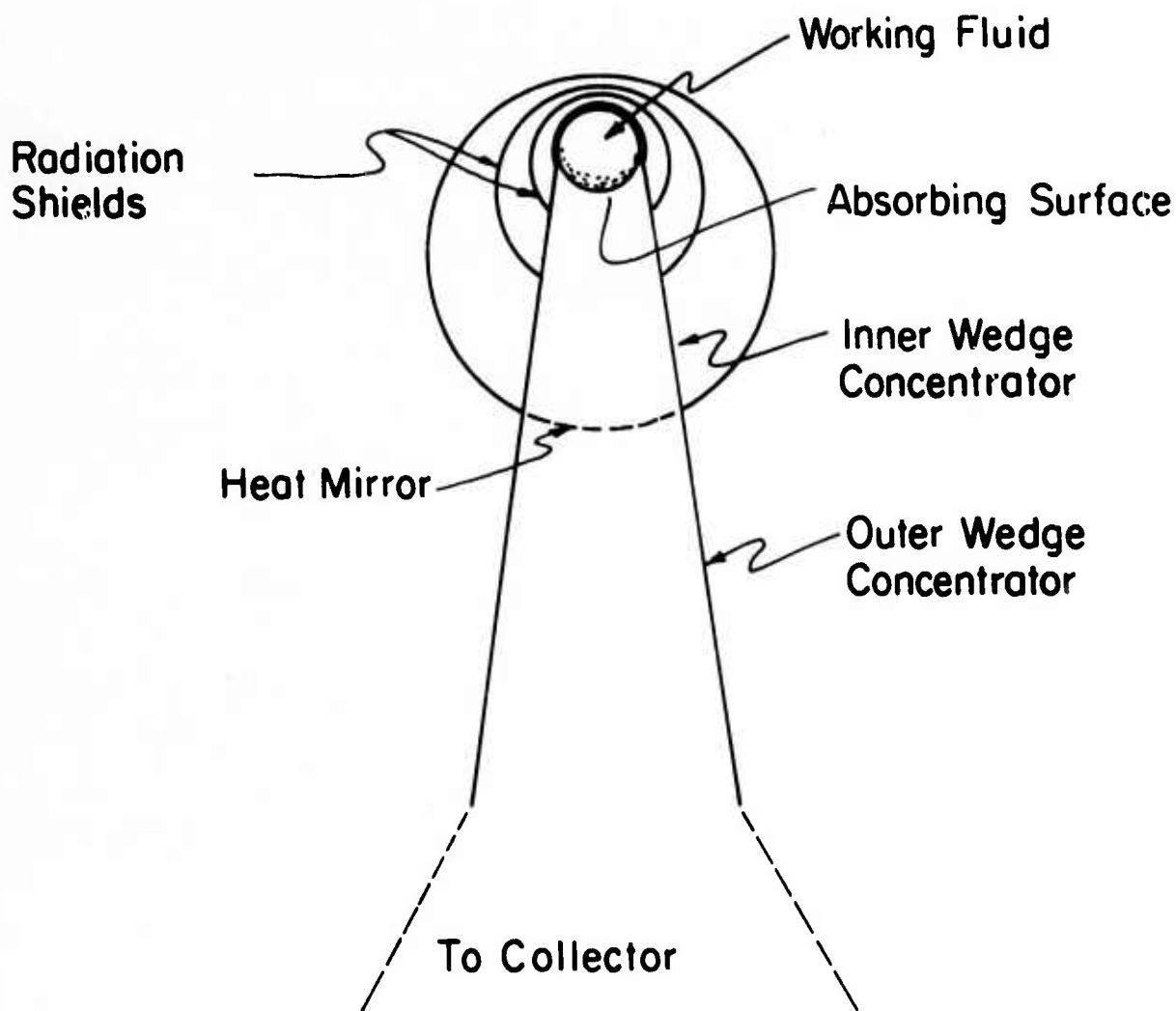
Figure 3.   Illustration of a solar energy collector with large concentration factor which utilizes an inexpensive aluminum foil wedge concentrator and radiation shields, as well as a heat mirror on the glass vacuum tube.

SPECTRAL PROPERTIES OF SMALL PARTICLE
METALLIC COATINGS,
I.   General Considerations

A. J. Sievers

Abstract

We find that in the free electron approximation, the
plasma resonance for small metallic particles can be adjusted
to occur near the center of the solar spectrum. A metallic
particulate coating is expected to be temperature independent
because the Fermi temperature of the electrons is extremely
large and the electron mean free path is determined by the
small particle size. A bright metal surface coated with this
material can provide a nearly temperature independent wave-
length selective coating for collectors of solar energy.

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SPECTRAL PROPERTIES OF SMALL PARTICLE
METALLIC COATINGS,
I.   General Considerations

A. J. Sievers

Introduction

The use of spectrally selective surfaces for collectors of solar energy in power generation systems have been proposed by Tabor[1], Shaffer[2] and Whitaker[3]. Maximum conversion of solar radiation to useful heat requires surface properties with a maximum total absorptivity, a, for solar wavelengths (0.3 to 2.0 microns) and a minimum emissivity, ε, for longer wavelengths appropriate to thermal reradiation (2 to 30 microns). In this paper we investigate the selective radiation properties of small particle metallic coatings.

Tabor[4] has divided the kinds of selective surfaces into two classes. The first class consists of a smooth low emissivity metal base covered by a thin surface layer which is visibly dark but substantially transparent in the infrared. The second class pertains to those systems which are entirely metallic so that the infrared emissivity is naturally low but because of color or a finely divided structure the absorptivity in the visible spectrum is larger.

-112-

Selection surfaces of the first class usually consist of a polished metal surface covered with a very thin layer of a black semiconductor, having a thickness around 10^{-4} to 10^{-5} cm. This black outer surface is about the thickness of one wavelength of visible light and absorbs the solar radiation. In the infrared the coating thickness is small compared to a wavelength so it is transparent and the emissivity is determined by the nature of the bright metallic surface under the coating. The experimental work on these coatings has been reviewed by Daniels[5]. Typically $\frac{a}{\varepsilon}$ ratios between 5 and 10 have been obtained using this technique.

A somewhat different approach first used by Edwards, et al. is to coat the surface with a thick (100 micron) film semiconductor (Si) coating. The absorption coefficient of a semiconductor increases greatly with increasing photon energy for energies near the band gap. The film is then absorbing in the short-wavelength (visible) region and is transparent in the long wavelength (infrared) region. Recently Seraphin[6] has obtained $\frac{a}{\varepsilon}$ ratios of 10 to 12 using this technique.

Another contribution to this class is based on the principle of the interference filter, in particular, interference effects in metal-dielectric multilayer stacks. A particularly promising interference stack has been developed by Schmidt and Park[7]. Again an $\frac{a}{\varepsilon}$ ratio between 10 and 20 is obtained.

As the temperature is increased for each of the coatings described above the $\frac{a}{\varepsilon}$ ratio decreases. At 300°C the $\frac{a}{\varepsilon}$ ratio typically decreases by a factor of two from the room temperature value. Moreover the multi-layered coatings have the additional problem that diffusion between layers occurs, eutectics form, and mechanical changes such as roughening or flaking have been observed.

These degradation factors will be kept to a minimum if a one component metallic selective surface of the second class is used. Little work has been done on such systems. Tabor[4] noted that polished zinc absorbs about 55% of the solar spectrum but has a low emissivity in the infrared. Irvine et al.[8] measured the selective radiation characteristics of fine metal mesh. They found an $\frac{a}{\varepsilon} = 2.2$ which was temperature independent up to 500°F.

A selective coating of the second class which has not yet been investigated consists of metal particles on a shiny metal substrate. It has been known for some time that small metallic particles have very different optical properties[9] than those of the bulk material from which the particles are made. In particular absorption bands[10-14] in the visible region of the spectrum have been identified with metallic colloids dispersed in various optically transparent media.

Because the Fermi temperature of the electrons in the metallic particles is much larger than the temperatures of interest and the mean free path of the electrons is determined

by the particle size, the optical properties of the metallic
particles remain temperature independent. A solar collector
consisting of metallic particles on a metallic surface would
have an $\frac{a}{\varepsilon}$ which is essentially temperature independent. In
addition, if the metallic particles consist of the same metallic
element as the substrate, the problems associated with chemical
and mechanical change would be minimized.

Small metallic particles can be routinely produced[15-17]
by evaporation of the bulk metal in argon gas at low pressures.
The size of the particles is controlled to a large extent by
the argon pressure.

These facts have provided the motivation for our in-
vestigation of the optical properties of a metallic particle
coating. In the next section we calculate the average dielec-
tric constant of the composite medium using the mean field approx-
imation. Then we calculate the optical properties when the
particles can be represented by a free electron gas approximation.
A resonance corresponding to the lowest frequency sphere mode or
the surface plasmon mode is optically active and can be adjusted
to the center of the solar spectrum. The composite medium is
transparent in the infrared region of the electromagnetic spectrum.

The Dielectric Constant of the Composite Layer

We start with a layer of nonabsorbing material with
dielectric constant ε_0 which contains a volume fraction f of

small absorbing ellipsoids with dielectric function $\varepsilon_1(\omega)$ as shown in Figure 1.

This composite medium is polarized by an external field E. The polarization in the medium can be described in terms of an average dielectric function $\bar{\varepsilon}$. If the field inside the ellipsoids, E_1, and the field outside the ellipsoids, E_0, are nearly homogeneous then $\bar{\varepsilon}$ is easily determined.

This homogeneous field approximation should be valid if the particles are much smaller than the wavelength of the electromagnetic wave. This allows us to neglect retardation effects inside the crystal and scattering[18].

It is also necessary that the metal composite should have a density $\leq 25\%$ of the density of the bulk metal. This latter condition comes about because the averaging process for the fields must be carried out over dimensions comparable to the wavelength of the radiation, i.e., the sample must contain many particles within λ. Therefore, for ellipsoids of revolution with axes a, a and b and for wavelength λ,

$$f \geq \frac{a^2 b}{\lambda^3} \tag{1}$$

To insure that the fields E_1 and E_0 have small inhomogeneities, the ellipsoids should be separated by a distance large compared to the mean diameter so

$$\frac{a^2 b}{\lambda^3} \ll f \ll 0.5 \quad . \tag{2}$$
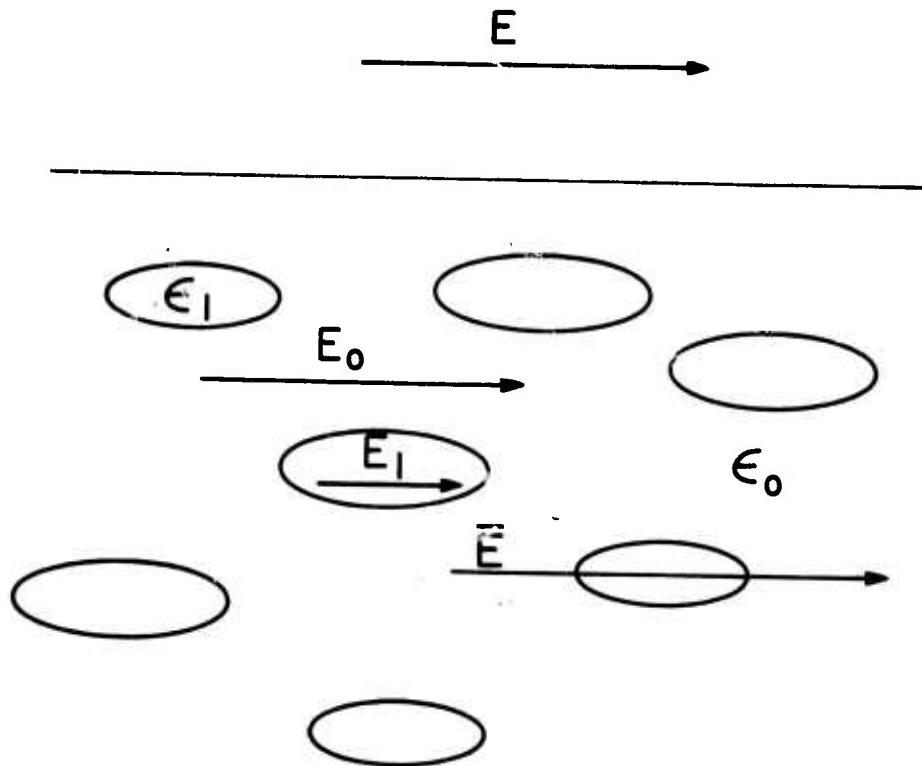
Figure 1. Metallic ellipsoids with dielectric function ε, embedded in a nonabsorbing medium with dielectric constant ε_0. The electric fields inside the ellipsoids are denoted by E_1 and in the nonabsorbing medium by E_0. $\bar{E}$ is the value of the electric field averaged over a volume containing many particles.

The average electric field, $\bar{E}$, inside the composite medium is assumed to be a volume average of the uniform fields E_1 and E_0 so[19]

$$\bar{E} = fE_1 + (1-f)E_0 \quad . \tag{3}$$

In addition, the average polarization inside the composite medium is defined as

$$4\pi \bar{P} = (\bar{\varepsilon}-1)\bar{E} \quad . \tag{4}$$

For particles with an ellipsoidal shape the average dielectric constant is[20]

$$\frac{\bar{\varepsilon}}{\varepsilon_0} = \frac{\varepsilon_0(1-f)(1-L) + \varepsilon_1[(1-f)L+f]}{\varepsilon_0[1-(1-f)L] + \varepsilon_1(1-f)L} \tag{5}$$

where L is the depolarizing coefficient which is a geometrical constant depending on the ratios of the axes of the ellipsoid. For any ellipsoid $L_x + L_y + L_z = 1$. For our case with the ellipsoid axes of revolution perpendicular to the surface $2L_x + L_z = 1$.

The Optical Properties

For small metallic ellipsoids the dielectric function of the bulk metal can be written as[18]

$$\varepsilon_1(\omega) = \varepsilon_\infty \left(1- \frac{\omega_p^2}{\tilde{\omega}^2}\right) \tag{6}$$
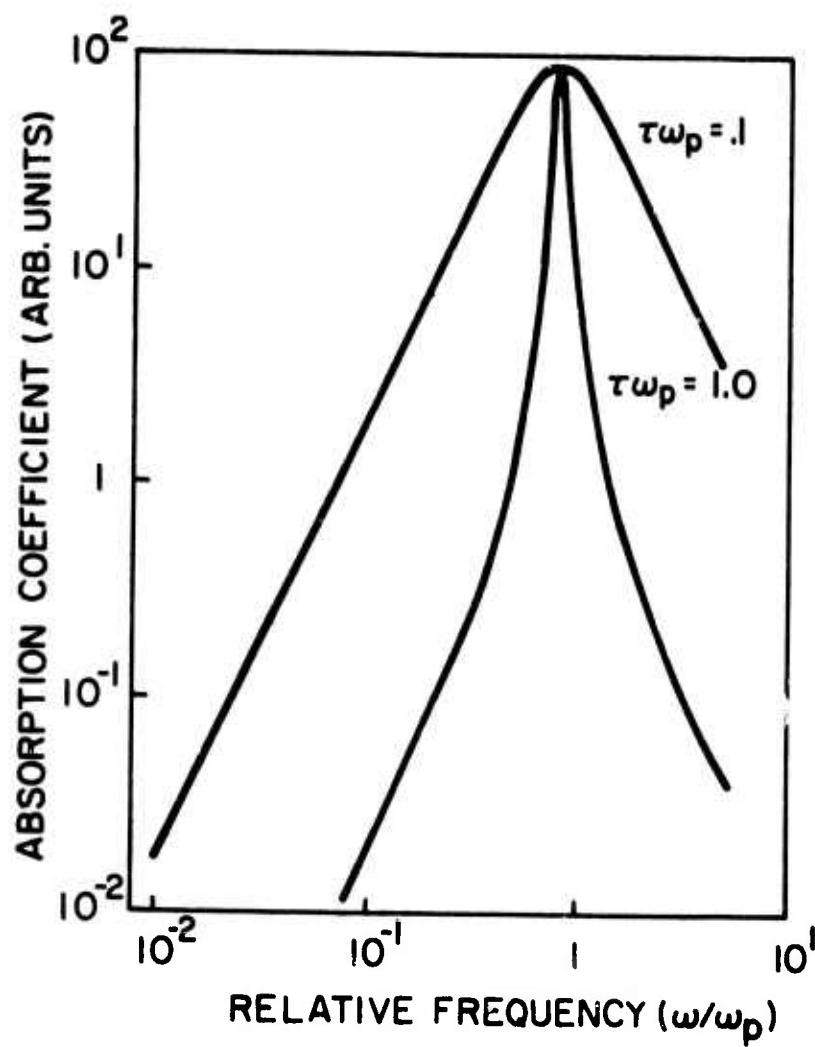
Figure 2. The frequency dependence of the absorption co-
efficient of a low density powder composed of
small metallic spheres. The relaxation time
has been indicated.

where

$$\omega_p^2 = \frac{4\pi Ne^2}{m^* \varepsilon_\infty} \tag{7}$$

and

$$\tilde{\omega}^2 = \omega^2 + \frac{i\omega}{\tau} \tag{8}$$

The expression for $\bar{\varepsilon}$ is obtained by inserting Eq. (6) into Eq. (5). We find that

$$\frac{\bar{\varepsilon}}{\varepsilon_0} = \frac{\bar{\varepsilon}_\infty}{\varepsilon_0} \left(\frac{\omega_h^2 - \tilde{\omega}^2}{\omega_\ell^2 - \tilde{\omega}^2} \right) \tag{9}$$

where

$$\frac{\bar{\varepsilon}_\infty}{\varepsilon_0} = \frac{\varepsilon_0(1-f)(1-L) + \varepsilon_\infty[(1-f)L+f]}{\varepsilon_0[1-(1-f)L] + \varepsilon_\infty(1-f)L} \quad ; \tag{10}$$

$$\omega_h^2 = \frac{\varepsilon_\infty[(1-f)L+f]\omega_p^2}{\varepsilon_0(1-f)(1-L) + \varepsilon_\infty[(1-f)L+f]} \tag{11}$$

and

$$\omega_\ell^2 = \frac{\varepsilon_\infty(1-f)L\,\omega_p^2}{\varepsilon_0[1-(1-f)L] + \varepsilon_\infty(1-f)L} \tag{12}$$

Note that Eq. (9) has a resonance when $\tilde{\omega}^2 = \omega_\ell^2$. For small damping $\omega_p \tau \ll 1$ and the resonance occurs at the frequency given by Eq. 12.

The damping of the resonance is determined by the mean free path of the carriers in the bulk for particle sizes greater than 200Å at room temperature. For smaller metallic particles

$\leq$ 00Å the mean free path is determined by the particle size itself and should be essentially temperature independent.

A Calculation with Spherical Particles

To estimate the frequency associated with the sphere mode we rewrite Eq. 12 as

$$\omega_\ell^2 = \frac{\omega_p^2}{1 + \frac{\epsilon_o}{\epsilon_\infty} [\frac{1}{(1-f)L} - 1]} \tag{13}$$

The plasma frequency for metals occurs in the UV part of the spectrum. To shift the sphere mode to the center of the solar radiation spectrum (1.8 eV) we want a material with $\frac{\epsilon_o}{\epsilon_\infty}$ as large as possible, a filling factor, f, as large as possible and L as small as possible. L is minimized for spherical particles where $L_x = L_y = L_z = \frac{1}{3}$ so we restrict ourselves to this geometry.

The bulk plasmon frequency, ω_p, for copper occurs at 7 eV[21]. For

$$\frac{\epsilon_o}{\epsilon_\infty} = 3, \quad f = \frac{1}{4} \text{ and } L = \frac{1}{3} \quad \text{then} \quad \omega_\ell^2 = \frac{\omega_p^2}{10}$$

so

$$\omega_\ell = 2.2 \text{ eV} \quad .$$

To decrease the frequency still further to $\omega_\ell = 1.8$ eV would require a filling factor $f = \frac{1}{2}$ in Eq. 13. It should be noted that our mean field calculation is not expected to be

very accurate for such large f values and it may be necessary to start with a metal with a somewhat smaller ω_p.

For a very thick layer of this composite medium electromagnetic radiation will be reflected between ω_ℓ and the ω_h given by Eq. 11. For our case we are interested in sufficiently thin layers so that most of the solar radiation is absorbed. The frequency dependence of the absorption coefficient of a low density powder composed of small metallic spheres for two different relaxation times is shown in Fig. 2. In 100Å copper particles $\omega_p \tau \simeq 0.1$.

Conclusions

Small metallic particles have a very different absorption spectrum than does the bulk metal itself. There exists no characteristic resonance for bulk metal because the transverse long wavelength motion of the free electrons has no restoring force. However, such motion in a small metallic particle results in a polarization charge at the surface which provides the restoring force needed to explain the resonant character of Fig. 2.

The resonant frequency is determined by the plasma frequency, ω_p, the filling factor, f, the depolarizing factor, L, and the dielectric constant in which the spheres are imbedded, ε_0. For the free electron model it is possible to tune the surface plasma resonance to the center of the solar spectrum by varying these parameters.

So far we have not considered the influence of inter-
band transitions on the optical properties of the composite
medium. In general, if the interband transition frequency occurs
below the plasma frequency then the absorption coefficient can
show both a resonance near the surface plasmon frequency as well
as an antiresonance near the interband transition frequency.
This latter frequency is somewhat temperature dependent and will
cause the absorption coefficient of the layer to be temperature
dependent. Whether or not this is a serious problem is yet to
be determined. Within the free electron approximation essentially
no temperature dependence (up to 300°C) in the absorption co-
efficient is expected because of the small particle size.

Acknowledgement

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CONCENTRATION, COLLECTION AND INSULATION

R. Kaplow

Although the total amount of sunlight falling on the earth each day is very great, the energy density (approximately 0.4 watt-hrs/cm^2/day[1] is significantly lower than is ordinarily utilized in the majority of extent energy conversion (e.g., to electricity) or utilization technologies. A number of the schemes proposed for solar utilization have therefore been based on methods for achieving a concentration of the sunlight energy prior to the actual utilization or conversion process.

In the designs for large thermal systems, the working heat transfer fluid could serve this purpose, collecting the heat from the sunlight over a large area and releasing it over the relatively small area of a heat exchanger of ordinary proportions. In principle, the heat transfer conduits could cover the entire collection area, and thereby accomplish the entire thermal concentration. However, it has seemed to a number of workers that it would be advantageous to concentrate the sunlight - as light - prior to its collection in any form. For thermal systems, this line of reasoning follows from two considerations.

1. The thermal insulation of the best collection and transfer conduits is imperfect (see later discussion). Therefore, if the area of those collector/conduits per unit of heat input is

reduced, the working temperature of the transfer fluid at the heat exchanger input will be greater. In principle, this leads to an effective use in the conversion process of more of the energy collected, due to the higher (heat engine) efficiency obtainable at higher working temperatures. In addition, reducing their area will tend to reduce the absolute amount of heat lost from the collector/conduits, providing the temperature dependence of the insulation is not overly disadvantageous. Even after an optimum temperature is reached (such as 500°C for a steam turbine) further concentration allows reduction of the size of the collector and so reduced radiative (and other) heat loss. These efficiency arguments apply particularly to large-scale electricity generating plants which would probably use steam turbine generators, but similar considerations apply to smaller systems, such as for home, office, and industrial space conditioning.

2. It may be more economical to concentrate the sunlight from a large area, as light, than to provide (and circulate) an equivalent area of active thermal collector/conduit. The economic considerations here relate to capital as well as to operational expenses. That is, the cost of constructing focussing mirror reflectors, for example, may be less per unit area than for collector/conduit and the operating costs (inclduing motions which may be necessary to maintain focus) may be less than the costs associated with the compensated fluid pumping.

The validity of the second type of consideration is not yet certain; indeed, for some of the focussing schemes which have

been suggested, the cost factors seem to be in the reverse direction. Also, it must be noted that with concentration schemes which depend on focussing light directly from the sun the potential advantages are significantly offset by the loss of the diffuse-sky light, which may average 50% or more of the total light available.

As regards direct conversion of sunlight to electrical energy, using photovoltaic cells, considerations of the type discussed in paragraph 1 above do not apply. Indeed, since the efficiency of such cells decreases with increasing temperature, one needs to dissipate the thermal by-product of the light absorbed. On the other hand, the present cost of photovoltaic cells (per unit area of coverage) is a dominant factor in considerations of their practicality for large-scale use. At the same time, it is known that existing quality cells can utilize about ten times the photon density of natural sunlight. Thus, low-cost light concentrators could make a significant impact on the economics of photovoltaic conversion. It is reasonable to expect, therefore, that the concentration of light will continue to be an important direction for investigation towards efficient and economical use of solar energy.

The achievable working temperatures and the effective utilization of the available sunlight are also strong functions of the collection and insulation parameters of the system. The thermal collector/conduit needs to abosrb all (or nearly all) of the sunlight falling on it (whether it sees the sky directly or

pre-concentrated light). Secondly, the collector/conduit obviously needs to be well insulated against conduction, convection and radiation losses. Moreover, the insulating system is subject to the constraint that it be transparent to the incident sunlight in the necessary transmission path (the actual path, of course, depends heavily on the design of the thermal collector and of the concentration system used, if any).

For thermal systems it appears that there is yet opportunity for significant design improvements regarding the basic configurations, regarding concentration, collection and insulation aspects in toto.

With photovoltaic systems, also, the absorption and retention of thermal energy are important factors - but in a reverse sense. Here the system design should allow only a minimal temperature rise. It is important to note, in this regard, that the major sources of the undesired thermal energy are the same phenomena that correspond to the major primary inefficiencies in the photovoltaic conversion of sunlight. In the ideal conversion process, a photon is absorbed through the excitation of an electron across an energy gap to a higher energy state, in which condition the electron can contribute to the current output by the cell. While significant practical inefficiencies exist for the internal process, the major inefficiency arises from the mismatch between the actual photon energies, and the energy required to excite electrons across the gap:

-128-

1. For a given photovoltaic material, many of the photons have insufficient energy for the electron excitation. These contribute nothing to the conversion process, but can generate heat, since the phonon excitation probabilities are not zero.

2. Photons which are sufficiently energetic will - on the average - over excite the electrons. That excess energy contributes nothing to the conversion process, but it again yields a temperature rise, through the thermalization by scattering of the "hot" electrons.

In this area as well then, detailed system design may be important to an efficient operation. The possibility of using multiple thin-cell "stacks", with each unit in the sequence utilizing a successively lower energy band of photons is discussed in the section which treats photovoltaic cells specifically. That scheme, if successful, would also obviate the thermal problem nicely. However, the attendant fabrication complexities - even assuming the availability of suitable energy gap photovoltaic materials - can only exacerbate the already difficult cost of cell production. An alternate design scheme - a combined photovoltaic and thermal system - would accept the type 2 inefficiency (above) in the photovoltaics, but would allow transmission of the lower energy photons to a thermal system below. Such a system seems particularly interesting for home/office use. In a third scheme, proposed by a group at the MIT Lincoln Laboratory, a sort of an inversion of the thermal/photovoltaic combination would be used[2]. The sunlight would be absorbed into a thermal reservoir first;

radiation (infrared) would be allowed to escape through windows in the insulation of the hot reservoir, through band-pass or high-pass optical filters selected to match the energy gap in photovoltaic cells positioned at the windows. These latter two concepts are subject to essentially the same considerations regarding concentration, collection and insulation as the purely thermal systems, with the additional constraints imposed by the required matching to the photovoltaic cell properties.

Design Details

1. Insulation and Collection

For high efficiency thermal systems, the primary insulation against convection and conduction losses most often considered is a vacuum, perfectly insulating for those two types of losses and perfectly transparent for the incident sunlight. For insulation against radiative losses, two directions seem obvious, and are being pursued. These involve the _optical_ properties of elements of the system for the specific radiation wavelength distribution that would be radiated by the hot collector/conduit:

        a.   To _reduce_ the emissivity of the hot surface, so as to minimize radiation emission [ε_{IR} should be small], and

        b.   To _maximize_ the reflectivity of an "envelope" (e.g., the inner surface of the vacuum enclosure), surrounding the hot collector, so that it acts as a perfect mirror for any emitted IR radiation [R_{IR} should be 1].

Both of these, however, need to be accomplished subject to constraints regarding the optical appearance of the surfaces to the wavelengths present in the sunlight.

      a.   The collector surface should be fully absorbing to the sunlight (i.e., α_{SUN} should be 1),

      b.   The radiation mirror should be transparent to the sunlight (i.e., T_{SUN} should be 1) at least in the optical path required by the geometry of a particular design.

In other words, for the hot surface one wants a large ratio, $\alpha_{SUN}/\varepsilon_{IR}$, and a large ratio for the infra-red radiation mirror, $T_{SUN}/1-R_{IR}$.

It is important to note that while these two approaches may be important individually, they do not add in a simple fashion to yield significant improvements as combinations. In other words, as the emissivity of the hot surface (ε_{IR}) is reduced to very small values, the effectiveness of the radiation mirror is lessened (if it is not a _perfect_ mirror) since any radiation reflected back is unlikely to be reabsorbed. On the other hand, a good infrared mirror can be beneficial when the ε_{IR} of the hot surface is not exceptionally small. This may be an important design consideration, since - from the materials point of view - it may be much easier to maintain desired optical properties of a surface at the low temperatures of a surrounding shield, than on the hot collector/conduit, assuming that the desired properties can be achieved initially.

-131-

There are a number of ways by which reasonably large values of $\alpha_{SUN}/\varepsilon_{IR}$ can be achieved, in principle.

    a. Coat a metal mirror-like surface with small particles ($\leq 1.\mu$). These do not couple with the long wavelength ($2-10\mu$) infrared radiation (characterisitic of a 600°C hot emitter) and the effective surface for the infrared is therefore the low emissivity substrate. The particles are relatively black to the shorter wavelengths ($0.3-1.0\mu$ in sunlight. CuO particles on aluminum, formed by spraying copper nitrate on Al sheet, has yielded $\alpha_{SUN} = 0.93$ and $\varepsilon_{IR} = 0.1$ for a ratio of 9.3 (at room temperature)[3].

    b. Coat thin films of materials which are intrinsic absorbers for short wavelengths on reflecting surfaces. Various semiconducting materials (e.g., silicon) have an optical absorption edge at about 1 micron of wavelength, just between the spectral distributions corresponding to sunlight on the one side and to the emission spectrum for a 600°C hot body on the other. Thus, a polished metal surface coated with silicon, and with the silicon in turn coated with an anti-reflective coating, will potentially yield high $\alpha_{SUN}/\varepsilon_{IR}$ ratios with a solar absorbance approaching 80%.[4]

    c. Coat a polished metal substrate with a series of layers using intrinsic and interference properties. A recent design has achieved an $\alpha_{SUN}/\varepsilon_{IR}$ of about 30, calcu-

lated for about 300°C (but with a solar absorbance of only ~77%). This was achieved as follows[4]:

Layer	Material	Thickness	Function
1	Mo	opaque	high reflectance in IR
2	Au	15 nm	high reflectance in IR
3	Al_2O_3	61.5 nm	reduce reflectance of short wavelength light by interference
4	Mo	very thin (semi-transparent	improve interference at Al_2O_3 surface <u>and</u> absorb sunlight
5	Al_2O_3	77 nm	protect last metal layer and provide additional interference type short wavelength absorption

None of these processes are trivial from the point of view of low cost fabrication; silicon coatings - made by chemical vapor deposition, may be the most economical and reliable. Further, we note that solar absortivities seem to be reduced (to about 80%) in achieving the highest $\alpha_{SUN}/\varepsilon_{IR}$ ratios, thus far. Most bothersome, however, is the probable instability of such coatings during long periods of duty at elevated temperature and with thermal fluctuations on a variety of time scales. From the materials point of view, there is concern about interdiffusion among film layers, and diffusion from the substrate (pipe) into the coating. A significant concern also exists regarding evaporation of surface elements (particularly if the surrounding insulation is a vacuum). In addition, thermal cycling, with its

attendant expansion provides additional constraints (expansion coefficient matching) on the properties of the useable materials.

For infrared mirrors, coatings of Sn_2O_3 and In_2O_3 have been suggested; with appropriate amounts of suitable dopant (Sb^+ and Sn^+, respectively) these both exhibit reasonably sharp reflectance edges near 1μ wavelength with high transmission in the visible region, and high reflectance for 600°C infrared. The best coatings yet developed are far from ideal however, with transmission coefficients for sunlight of only about 85%, combined with a transmission for the infrared of roughly 15%[5]. There appears to be a good deal of room for improvement, therefore, in the $T_{SUN}/(1-R_{IR})$ ratio, especially since the long term degradation of such a mirror should be less severe, because of its lower operating temperature. The physics behind such radiation shields is relatively straightforward: one needs to find a material in which (1) the excitation of phonons by the visible (Sun) light is slight and (2) there is a low probability for exciting electrons individually to higher energy states by amounts ≥ 1 ev, and (3) there is a sufficient density of carriers to yield a "plasma frequency" corresponding to $\sim 1\mu$ wavelength photons, with only longer wavelengths being able to cause such excitations. At the same time, the quality for the present purpose of the materials already known to be more or less suitable depends on metallurgical-like details. For example, the sharpness of the change in reflectivity is very dependent on the carrier

mean scattering time, a parameter known to be dependent on the density of structural defects.

It is interesting to note that contrary to one's initial intuition, high α/ε systems may be most useful in relatively low temperature systems. This arises both because it is easier to achieve a high ratio for the more widely separated radiation distributions, and because the complicated, high α/ε materials are likely to be more stable at low temperature. At the same time, it appears that high working temperature systems can be achieved even with low α/ε, given adequate solar concentration ($\sim$10-20$\times$).

In the light of these points, and the preceding discussion, we recommend a three-pronged materials development program, in associated with the radiation insulation aspect of the insulation, which appear to represent achievable goals. These are:

    a.   Develop surfaces with very high $\alpha_{SUN}/\varepsilon_{IR}$ ratios, with α_{SUN} as large as possible (>0.9), fabricable at low cost and using elements not in short supply; relatively low operating temperatures ($\leq$300°C) should be regarded as an acceptable goal for these surfaces.

    b.   Develop surfaces with moderate $\alpha_{SUN}/\varepsilon_{IR}$ ratios (e.g., 2-5), but with high durability at high temperatures ($\geq$500°C).

    c.   Develop surfaces with high $T_{SUN}/(1-R_{IR})$ coefficients, to be used as radiation mirrors in combination with

low α/ε collector/conduit surfaces. Development
of a radiation mirror surface of sufficiently high
performance would, in fact, eliminate the need for
the developments suggested under (a) and (b), above.

Needless to say, it would be desirable to avoid the use
of vacuum as part of the insulation in thermal solar systems.
It follows, therefore, that it would be desirable to develop a
material or material composite with exceedingly low conductive,
convective and (infrared) radiative heat transfer* coupled with
high sunlight transmissivity. At this point, however, it is not
obvious that such a development is possible, nor is it obvious
what research directions are likely to be fruitful.

2. Light Concentration

A variety of lens and mirror schemes are under discussion
and some have been constructed - at least in trial form. At the
present stage, it appears that mirror focussing systems will be
much less expensive to fabricate, install and maintain than lenses.
From the design point-of-view, it seems intuitively desirable that
when motion of parts of the system are required to maintain focus,
it is preferred to move as little mass as possible and as little
of the primary reflection area as possible. For high concentration
systems, it follows that the mirror - assuming that mirrors will
be used - should be stationary; indeed on the ground, so as to

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*Again, the low infrared radiative transfer aspect could be
 handled by a separate, high-performance radiation mirror.

-136-

avoid the need for a support structure. The Gulf General Atomic Corporation, according to a presentation made to the Workshop by John Russell, is giving serious consideration to such a scheme, in which individual flat mirrors are located on part of a cylindrical surface, and oriented to reflect the sun's rays into a region on the far side of the cylinder. This provides a two-dimensional focus onto a collector/conduit pipe, which moves to track the sun's image.

It does not appear that materials per se will be a fundamental determinant of the engineering and economic feasibility of the light concentration aspect of such systems. To be sure, attention will have to be paid to the durability (or inexpensive replacement) of mirror surfaces, and to the choice of materials for the conduit/pipe and vacuum enclosure (if one is used); but it does not appear that the probability of achieving successful and economic installations of large thermal systems (to generate electricity or a secondary fuel, such as hydrogen) will be determined (or even much affected) by new materials development for this aspect of the system. Rather, this concentration part of the problem seems most likely to benefit from advanced and inventive basic design developments and creative notions for such things as on-site fabrication schemes, modular prefabrications, etc.

The fluctuations in solar input lead to the requirement that a large plant - if it is to provide a fairly uniform electrical output - will need not only a large storage capacity, but

also a momentary power capacity perhaps 5× the average output; it is particularly important that the design of such plants be considered with the storage (or secondary fuel generation) and the input variations as primary aspects - rather than an addendum. From the design point-of-view, it should be mentioned that consideration should also be given to <u>utilizing</u> the radiation "losses" to the cold night sky; thus far, this phenomenon has been considered only as an efficiency loss.

Acknowledgements

A MEMORANDUM ON THE SUBJECT OF
PHOTOVOLTAIC SOLAR ENERGY CONVERSION

J. J. Loferski

1. The photovoltaic effect, i.e., the generation of an emf
as the result of the absorption of light, is very common in semi-
conductors. It is a minority carrier phenomenon. The existence
of a photovoltaic effect requires the presence of an electric
potential barrier in the region where mobile carriers are pro-
duced as a result of light absorption. The lifetime of the
minority carriers must be large enough to allow them to diffuse
to the barrier. The barrier can be a p-n junction incorporated
into a single semiconductor (a homojunction) or a p-n junction
in which the p-semiconductor is a different material from the n-
semiconductor (a heterojunction) or it can be a Schottky barrier.
The theory of p-n homojunction cells is well developed and the
behavior of such junctions is predictable and in conformity with
experiments. The theory of p-n heterojunction cells is poorly
developed and it is difficult to test such cells experimentally
because of the complexity of phenomena which are involved, i.e.,
lattice mismatch leading to interface states, possibility of
tunneling through potential barrier "spike" at interface, the
role of electron affinity in determining the band-matching at
the interface, etc. The theory of Schottky barrier photocells

is also poorly developed and difficult to apply because of the role of surface states, oxide layers, etc., on real surfaces, the real properties of thin metal films, etc.

2. According to the theory of p-n junction photovoltaic solar energy converters, the maximum efficiency which can be attained in a single p-n junction cell is about 25% for air mass zero (AMO) sunlight illumination. Such efficiency should be attainable in a semiconductor with a band gap of about 1.5eV. The band gap is a first order parameter in determining the upper limit on efficiency of a cell. The curve of maximum efficiency vs. energy gap passes slowly through its maximum; energy gaps between 0.9eV and 2.5eV have upper limits on efficiency in excess of 15% on the assumption that the p-n junction behaves in accord with the classical Shockley theory. If the Shockley theory is not obeyed, e.g., if recombination and generation occurs in the space change region, the maximum efficiency decreases to a value between 15 and 20%. The efficiency is a function of spectral composition of the incident sunlight so that it varies with time of day, season of the year, etc.; these variations can amount to a few percent.

3. The main loss mechanisms are photons whose energy is too small to generate hole-electron pairs (in Si, 24% of AMO photon energy is rejected for this reason) and photon energy in excess of the band gap (in Si this loss amounts to 33% of AMO photon energy). The magnitude of these two losses are set once the

semiconductor is selected. It is possible to reduce the second
loss by making tandem cells, i.e., an arrangement in which a group
of cells made from materials of varying energy gaps are placed on
top of each other in order of descending energy gap. In such an
arrangement, the light strikes the first (largest) band gap cell
and the radiation corresponding to smaller photon energies than
the band gap energy is transmitted to the next cell in the tandem
arrangement, etc. If the minimum band gap in the sequence is
1.1eV (the band gap of Si), and if the other characteristics of
the junctions are similar to those of the best currently available
Si cells (14% efficiency), then the maximum conversion efficiency
for the tandem cell arrangement would be about 25%. If the
characteristics of the junctions could be made equivalent to those
required of the improved Si solar cell which is expected to have
efficiency of 22%, then the maximum conversion efficiency of the
tandem cell structure would be about 38%. Such arrangements other
than single homojunctions may become practical if cells of sub-
stantially reduced cost become available in a number of materials
of various energy gaps.

4. Currently in the U.S. (and indeed in the world) there is
available commercially only one kind of solar cell, namely the
single crystal silicon p-n homojunction cell. This cell has been
the "backbone" of the space power program. It is the source of
on-board power for virtually all unmanned space satellites and
for the manned space laboratory program. Its operation is well

understood because it is a homojunction. It has an air mass
zero (AMO) efficiency of about 11% in commercial cells but it is
confidently expected that efficiencies in the vicinity of 20%
should be attainable (laboratory cells having AMO efficiencies
of 14% have already been made). The only market for these cells
has been in the space program which requires an annual production
of cells capable of producing an output between 50 and 70 kW under
constant illumination in outer space. Because of the emphasis on
reliability and relatively small contribution (a few percent) of
solar cells to the overall cost of a space mission, there has
been minimum incentive to reduce the cost of silicon cells for
space application and therefore the cost is artificially high.
Obvious changes in manufacturing procedures and design of silicon
cell arrays intended for terrestrial applications would reduce
the price of silicon solar cell arrays to the range of about $70/m^2
according to estimates of U.S. solar cell manufacturer (Spectrolab
Division of the Textron Corp. and Centralabs). New methods for
making ribbons of single crystal silicon and for doping cells
currently under investigation would if successful lead to arrays
in the range of about $25/m^2. It does not seem possible to achieve
lower costs than this with already identified technology, i.e.,
without unpredictable "breakthroughs".

The amount of money invested in research and development
on silicon solar cells during the past decade has been about $1
million dollars/annum. The sources were NASA and the Air Force

whose main concern was with increased radiation hardening. There has been virtually no investment in research by private industry because the total volume of sales of solar cells never has exceeded $10 million dollars/annum divided between two or more manufacturers. Large scale terrestrial applications were not seriously explored because the conventional wisdom assumed that nuclear power was the solution to the electrical power needs of the world.

5. The photovoltaic solar cell system which after silicon has been most intensively studied is the Cu-CdS thin film solar cells. Research and development on this system consumed about $1 million dollars/annum for about ten years; the work was sponsored by NASA and the Air Force who hoped to be able to use this system in space. The potentially higher watts per pound from Cu-CdS thin film cells were a principal cause for interest in this cell as a replacement for silicon.

The cell was in pilot production at Clevite for a number of years, but support for the program was cut-off about four years ago because it was not possible to eliminate degradation of the output of the cell with time (on a scale of years) and because the efficiency ($\leq$ 5%) was not adequate for space applications.

Work on this system has been recently revived (mainly at the University of Delaware) by RANN-NSF because the cost of such cells promises to be lower than that of silicon single crystal cells. Economic analyses of this system by representa-

tives of the Dupont Company and by chemical engineers at the University of Delaware predict that the cost of arrays of Cu-CdS thin film cells would be in the range of $10/m^2$ if the volume were at least $8\times10^7 ft^2$/annum (about 3 miles^2/annum). However, neither Dupont nor any other manufacturer is prepared to begin production of the cell unless there is confidence that the degradation problem has been solved and that the finished product will therefore have a large market.

6. Single crystal p-n homojunction solar cells have also been made from the III-V semiconductors GaAs, InP and the II-VI semiconductor CdTe. The most intense effort was that applied to GaAs cells which attained efficiencies of about 10-11% in 1961. About $1 million was spent on the GaAs cell program. It was abandoned because it was estimated that GaAs single crystal cells would cost at least a factor of ten more than silicon cells. (It has been reported that the USSR has used GaAs single crystal cells to power some of its satellites.) The InP effort was very small and resulted in efficiencies of about 8%. It is interesting to observe that no major research and development effort has ever been mounted with the goal of producing semiconductor material specifically for solar cells. Solar cells from Si, GaAs, InP, CdTe and Cu-CdS all depended on other potential commercial applications for these electronic materials. The reason for this lack of interest has been the lack of any substantial market for solar cells.

Recommendations for Future Work

1. Large scale terrestrial application is impeded mainly by the cost of solar cells and solar cell arrays. The thin film Cu-CdS solar cell system seems to promise a favorable low cost but it has technological deficiencies. It is recommended that major emphasis be placed on understanding the photovoltaic process and degradation mechanisms in this system. There are many recently developed tools for exploring thin films like those of Cu_xS on CdS, techniques like Auger electron spectroscopy, ion spectroscopy, secondary electron emission spectroscopy, etc. There is reason to believe that it may never be possible to stabilize Cu_2S because the copper which is interstitial is very mobile in this material.

2. The cost of growing single crystals is a serious impediment to producing single crystal silicon cells at a cost as low as that projected for thin film Cu-CdS cells. Therefore, major emphasis should be expended on exploring the possibility of making say 5% efficient silicon cells from polycrystalline silicon. The transmission of minority carriers through boundaries requires exploration. The conventional wisdom assumes that minority carrier diffusion lengths of the order of 50 microns are required in silicon cells and this presumably implies grain sizes of this dimension in useful polycrystalline silicon cells. These assumptions should be tested experimentally and explored theoretically. New ways to grow single crystals should be sought. Ways to deposit Si on inexpensive substrates and to produce single crystal

"grains" of sufficient area for acceptable efficiency solar cells are needed.

3. Achievement of high efficiency solar cells is not as high a priority item as the production of low cost solar cells. However, the possibility of achieving efficiencies of 20% in AMO sunlight should be explored. This will require preparation of single crystal silicon having minority carrier diffusion lengths of $\geq$ 100 microns in material of 0.01 ohm cm resistivity and the control of surface electronic properties so that a surface recombination velocity of $\leq$ 100 cm/sec can be maintained on Si crystals of 0.01 ohm cm resistivity.

4. Research should continue on other materials though at a lower level than that expended on items 1 and 2 above. The emphasis should be on materials which are favorable for thin film cells, i.e., direct gap semiconductors. The band gaps should be in the range 0.9 to 2.5eV.

5. Schottky barrier and heterojunction cells should be explored because fabrication of such barriers seems to promise lower cost than fabrication of p-n homojunctions.

6. The support level for solar energy research should be increased to conform more closely to the sums recommended by the NSF-NASA panel on Solar Energy.

Acknowledgement

PHOTOVOLTAIC DEVICES: A DISCUSSION SUMMARY

H. Ehrenreich

Following the meeting on solar energy, a group consisting
of R. Bleiden, M. Cohen, H. Ehrenreich, R. Huggins, W. Kohn,
R. Kaplow, and J. Loferski discussed the general subject of photo-
voltaic devices as an energy source. This note attempts to
summarize that discussion. While the comments in their present
form are the results of a group effort, some viewpoints expressed
here may not necessarily be shared by all participants. Further-
more, in view of the informality of the discussion, there may be
some points of inaccuracy of fact or emphasis.

General Comments

The emphasis of future solar cell research should empha-
size terrestial rather than space applications. Low efficiencies
($\sim$5%) and less reliability can be tolerated in the case of
terrestrial uses, and as a result the cost should be lowered
appreciably. To be economically competitive with other energy
sources, the cost must be $\sim$\$3-20/m^2, depending on the specific
application.

A factor of ten reduction in crystal Si solar cell cost
is possible without a breakthrough in the existing technology.
One foot wide single crystal ribbons have been produced at Tyco

and Westinghouse. However, since a reduction of about 100 in cost is required for electric power generated by photovoltaic cells to be competitive with that generated by fossil fuel or nuclear plants, where seems to be no large identifiable market for such cells. (Toys and digital clocks have been considered in this connection.) The group guessed that of the order of ten million dollars of R&D expenses would be required in order to make mass production possible.

It was not clear to what extent the use of polycrystalline Si films had been investigated. Such films would be cheaper on the one hand, but less efficient on the other. It would seem important to develop more information concerning this point.

The use of heterojunctions, and in particular the Cu-Cd-S system was also considered. One general advantage of hetero-junctions (which emerged in later conversations with Eden and Joseph of North American Rockwell) is that sunlight can be sent through the larger band gap transmitting layer and absorbed in the narrower band gap depletion region in the junction. This procedure minimizes the electron-hole recombination. This is not the mode in which the Cd-Cu-S cells are used, presumably because of the way they are manufactured (CdS is the substrate material; a thin CuS_2 layer is chemically produced).

It appears that the presently existing Cu-Cd-S devices have been produced using a great deal of empiricism. The funda-mental knowledge concerning their operation is far below that of Si. (The theory of heterojunctions in general is considerably

less developed than that of homojunctions.)

Present efforts to develop such devices are centered in the laboratories of Boer, Bube, and Loferski located respectively at the University of Delaware, Stanford, and Brown University. The total funding amounts to about $425K with the largest portion going to Delaware. The Stanford effort is just in its beginning stages. Clevite was supported by NASA and Air Force programs to develop thin film cells for about ten years at the rate $\sim$\$400K per year. This program was terminated about three years ago because no <u>space</u> applications seemed probable. The achieved efficiencies are generally in the range 2-5%, although occasionally 8% has been obtained on cells which degrade unacceptably with time. Indeed, photodegradation seems to be a universal problem. Roof-top tests at Delaware have shown that some degradation is healed at night: the cells may recover to some extent when illumination ceases.

The fact that Cu diffuses rapidly in CuS_x may not have been emphasized sufficiently. The diffusion in the α-phase has the same order of magnitude as in liquids above the phase trans-formation temperature (91°C). In view of the deleterious effects of Cu in other semiconducting systems (recall, Cu was the original transistor "deathnium"), it would seem appropriate to question the use of Cu based systems in photovoltaic applications.

Several homojunction systems involving compound semi-conductors have been considered. A program at General Electric developed a CdTe solar cell. CdTe is attractive because its band

gap of 1.5 eV is close to that corresponding to maximum efficiency for the solar spectral distribution. The achieved efficiencies were 8% for single crystals and 5% for thin films. Unfortunately, degradation was found to occur, as in the Cu-Cd-S system. This material would probably not be suitable for terrestrial uses since $\sim$80K tons of Te would be required over a ten year period in order to fulfill U.S. needs, whereas only $\sim$200 tons per year are currently available. A question concerning the adequacy of the Cd supply was also raised. Apparently the CdTe activity was terminated because a larger investment had already been made on the Cu-Cd-S system and there appeared to be no clear-cut incentive for preferring one system over the other.

Other homojunction systems, such as the ternaries $CuInS_2$, $AgGaSe_2$ were investigated because they have nearly optimal band gaps and because of certain analogies to the 2-6 compounds.

Schottky barrier diodes also produce a photovoltaic effect. The ternaries $CuGaSe_2$ and $CuGaTe_2$ operate in this manner.

While in an ideal sense ternary compounds offer a great richness of possibilities, in terms of tailoring band gaps, depletion layers, mobilities, etc., they also pose genuine compositional control problems. From the stochiometry standpoint it would therefore appear desirable to use homojunctions containing as few constituents as possible. This view would imply that Si is preferable to GaAs, and GaAs, in turn is preferable to Cu-Cd-S. It may be that better materials preparation techniques as well as deeper understanding of heterojunctions may alter this view.

U. S. Competence in Photovoltaic Field

In industrial laboratories the capability for effective R&D activities certainly exists, but it is not being utilized, presumably because the immediate economic incentives are lacking. There are many university laboratories having a supercritical semiconductor effort and requisite crystal growing facilities. Those having associated Material Research Laboratories, such as, for example, M.I.T., Stanford, Harvard, Purdue, and Brown, could acquire competence in this field very quickly given adequate financial resources. Presumably also, if the AEC Laboratories indeed become the core of the energy R&D agency, a significant proportion of research will be done in those institutions.

Fundamental Questions

The present discussion group regarded the following questions as significant topics for further fundamental investigation.

In connection with Si photovoltaic devices, the effects of clean grain boundaries on the efficiency should be investigated. It would seem desirable to have systematic experimental investigation involving bi and tricrystals, to identify orientation effects, as well as precipitation and recombination sites. Diffusion effects along grain boundaries could be examined by constructing junctions using either ion implantation or codeposition techniques. The understanding of such diffusion effects are important particularly in polycrystalline junctions since diffusion might short circuit them.

This leads to the question of the general usefulness of polycrystalline materials and their general limitations. Why, for example, are they satisfactory for the Cu-Cd-S system and seemingly not for Si? It may be that polycrystalline Si has not yet been sufficiently investigated in order to form a clear judgment.

In connection with the Cu-Cd-S system, it would seem important to understand the nature of the degradation phenomena more clearly. These may conceivably be connected with grain boundary precipitation, random precipitation, Cu diffusion into CdS, and Cd diffusion into Cu_xS.

Since heterojunctions in general may also be of practical usefulness in solar energy conversions, it would seem important to ask whether the present fundamental understanding of such devices is adequate for possible photovoltaic cell applications. Deeper insight into the workings of these devices might permit a more systematic search for candidates other than Cu-Cd-S. Another question concerns the desirable properties of electronic structure of the substrate. More generally, one might ask whether the photovoltaic process in heterojunctions is the same as in homojunctions. It is, for example, possible to make Schottky barrier devices in heterojunctions. Possible advantages of such devices should be investigated.

PHOTOCHEMICAL PROCESSES AND
SOLAR ENERGY UTILIZATION

J. C. Light

The direct utilization of solar energy for production
of fuels (other than the biological conversion) has been con-
sidered and, as with all other large scale processes, rejected
over a number of years. The purpose of this brief paper is to
outline the possibilities, practicalities and prospects of the
general problem of non-biological photochemical conversion on
a large scale.

There are (at least) three general modes of utilization
of solar energy in chemical conversion that one can consider.
They are

(a) Direct photoinduced and endothermic chemical reactions
at low temperature ($280°K \leq T \leq 400°K$) in which the products
of the reaction can be stabilized against the reverse
(exothermic) reaction until desired. Such photochemical
processed would store energy, occur at low temperature,
and be reversible under appropriate conditions to release
either thermal energy or electrical energy in a fuel cell.

(b) Direct photogalvanic production of electrical power by
means of the EMF produced by the non-equilibrium (thermal)
stationary states which can occur between illuminated and

-153-

dark electrodes in appropriate electrolytes.

(c) Combined solar energy driven thermal conversions (perhaps photochemically assisted) which may occur in the appropriate high temperature ($400°K \leq T \leq 1000°K$) solar energy conversion cells. The possibilities for this range from energy storage in a simple phase transformation (eutectics or vaporization for example) to high temperature photo-assisted endothermic reactions in which the products are quenched and stored.

It should be noted that processes of types (a) and (b) are non-equilibrium stationary state threshold processes whereas process (c) is at least a mixed thermal and photochemical process. Processes (a) and (b) differ in that process (a) produces, under illumination, a chemical fuel which must be separated and stored, whereas process (b) produces directly electric power which might be stored in batteries. Process (c) produces thermally equilibrated products, the energy of which may be stored in four possible ways - by inhibition of back reaction as the temperature drops (quenching) by physical separation, by storage of thermal energy in high temperature sinks such as "pebble beds" or other thermal sinks, or, more indirectly, by generation of power and storage of electricity in batteries.

Since these possibilities have all been touted at one time or another it may be useful to consider the practicalities of solar energy itself before concentrating on what is known and the prospects of each area separately. To this end we note the

facts (a la 1973) about the solar energy spectrum (presumably
unchanging) and the economies of alternative sources of power
(which may change by an order of magnitude in 30 years). Currently
gasoline is ~$.5/gal and milk is $1/gal. The energy content of
gasoline is ~4,000 times that of milk. This in terms of energy,
gasoline (etc) is at least three orders of magnitude cheaper than
animal biological products, and roughly two orders of magnitude
cheaper than vegetable biological products per calorie. At current
energy prices, each square foot of sunny land is worth ~$0.10 to
$0.20/year in total incoming solar energy, or roughly $600/acre.
Since crops at current prices are worth up to ~$200/acre, the
question of cost looms very large. Presumably arid sunny land
from which solar energy is easily useable form can be sold for
~$.15/ft²-year is economically very feasible now and may be worth
a factor of 3 times this in the next decade. However, it is not
clear that such low costs are feasible with current technology.

The solar spectrum, although roughly that of a black body
at 6000K, is rather flat in the visible range and has a very sharp
drop for wavelengths (λ) less than ~3300Å, primarily due to the
ozone layer of the upper atmosphere. The maximum efficiency of
photochemical processes (a) and (b) is sharply limited because
they are threshold processes which can use only a fraction of the
solar energy. Photons of energy lower than the threshold energy
(E_T) cannot cause the reaction to occur, and those photons absorbed
with energy above the threshold may cause the reaction but have
only a fraction of their energy stored. In addition the processes

-155-

in which the change in free energy is significantly less than the change in enthalpy or heat content.

This is illustrated roughly in Figs. 1 and 2. Figure 1 is the number of photons per cm^2-sec (at normal incidence at the equator) of wavelength $\lambda < \lambda_T$. If each photon of energy $E > E_T$ absorbed leads to an entothermic chemical reaction with quantum efficiency $\phi(E)$ in which an amount of energy E_S is stored in chemical energy, then the amount of energy stored chemically/cm^2-sec is

$$E/cm^2\text{-sec} = E_S \int_{E_T}^{\infty} N(E)\phi(E)dE$$

where $N(E)$ is the number of photons per unit energy range per cm^2-sec. The threshold energy, E_T, must exceed E_S, i.e., $E_S = E_T - \delta$. Assuming unit quantum efficiency we may plot E as a function of E_T and δ. This is given in Fig. 2. It can be seen that the optimum threshold energy must lie near 2 eV and that δ must be less than 1 eV in order for efficiencies to be of the order of 15% or larger. In fact only one reaction is known (to me) in which this is approached and in this case the free energy change is much less.

Similar considerations apply to photogalvanic cells although in this case the entropy losses may be much smaller. (However the quantum efficiency rarely approaches unity in the condensed phase.) These considerations do not apply to the third case in which the chemical equilibrium is essentially maintained and the energy of all photons absorbed can be used to drive the

endothermic reaction.

With these general considerations in mind we shall look at one example of each type and then give some suggestions of problems and possibilities for further research.

A.   Direct Photochemical Reaction for Fuel Production

This type of process must involve at least four steps:

1) Absorption of radiation

2) Rapid stabilization by net endothermic reactions

3) Separation of high energy products for storage

4) Recombination of fuels under conditions appropriate to energy utilization

In this mode of utilization of solar energy it is necessary to prevent the thermalization of the absorbed energy, i.e., a "photochemical diode" is required in step (2). There are at least three mechanisms by which this can occur:

1) Utilization of the differences in kinetics of two and three body reactions in the gas phase. (The NOCl system could depend on this.)

2) Utilization of the differences in reaction cross sections when energy is in different degrees of freedom.

3) Utilization of differential solubility (or other phase separation) of products to inhibit back reaction (i.e., combining steps 2 and 3).

An example, the most optimistic known to date, of the first mechanism is the following gas phase reaction

$$NOCl + h\nu(\lambda < 6500\mathring{A}) \rightarrow NO + Cl$$

(Abs. coeff. $\alpha \sim 10$ liter cm^{-1} $mole^{-1}$)

$$Cl + NOCl \xrightarrow{k_1} NO + Cl_2$$
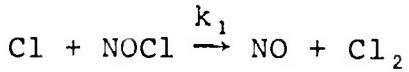
$k_1 \sim 1 \times 10^{13}$ $e^{-1,060/RT}$ cm^3 $mole^{-1}sec^{-1}$

Net reaction: $2NOCl + h\nu(E_T = 1.6$ eV$) \rightarrow 2NO + Cl_2$
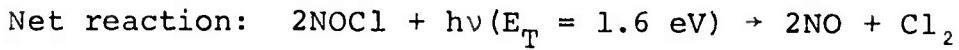
$\Delta H^\circ_{298} = 18.4$ kcal/mole, $\Delta G^\circ_{298} = 9.8$ kcal/mole.

The kinetics of the reverse reaction have been well studied, and it is a termolecular mechanism

$$2NO + Cl_2 \xrightarrow{k_r} 2NOCl$$
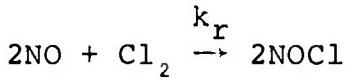
$k_r = 3 \times 10^{11}$ $e^{-6,000/RT}$ cm^6 $mole^{-2}$ sec^{-1}

The chemical energy stored per photon absorbed is $\sim.80$ eV, and the maximum efficiency of solar energy storage by this process is roughly 20%. However, the free energy storage at atmospheric pressure is only half that value, and at lower partial pressures is smaller yet.

The reverse reaction is quite slow, requiring roughly 10^3 seconds at T = 300K and partial pressures on the order of .4 atm NO (1 atm total). Thus the second step of the photochemical scheme is an effective diode, allowing sufficient time for separation. The third step, separation, also appears possible by differential solubility in solvents such as S_2Cl_2 (b.p. 138°C) or CCl_4 (b.p. 77°C) which preferentially dissolve Cl_2 (in S_2Cl_2)

or Cl_2 and $NOCl(CCl_4)$. Finally, the Cl_2 (and NOCl) may be extracted from the solvent by gentle heating and the NOCl separated from the NO (or Cl_2) by condensation (NOCl b.p. $\sim -10°C$). The net result of this would be the production of NO and Cl_2 at .1 to 1 atm pressure with a net free energy storage on the order of 5-9 kcal/mole Cl_2 and overall efficiency of free energy stored/energy of solar radiation incident of roughly 5-10%.

The last step, however, is difficult. Even with catalysts, at low pressures NO and Cl_2 recombine significantly to evolve heat only at temperatures up to $\sim 300°C$. Thus the thermodynamic efficiency will drop to $\sim 2-5\%$ in terms of electrical energy production/unit solar energy. In a fuel cell Cl_2 and NO generate $\sim .2$ volt.

It is worthwhile to list some of the assets and liabilities of this system. Under assets we have:

1. Products photochemically stable (Cl_2 dissociation will also produce NO and Cl_2 in subsequent reaction)

2. Threshold near optimum

3. Separation apparently feasible

Under liabilities we have:

1. Recombination difficult - low temperature fuel

2. Corrosive chemicals must be handled

3. Free energy change lowered by dissociative process

In this area there are a few of other systems which might be examined: S_2Cl_2, $HgCl_2$, $NO_2-N_2O_5$, etc., but the requirements are rather rigid - an unstable molecule must absorb light and

react to form even more unstable molecules which can be separated.

The efficiency would be greatly improved if the entropy change between reactants and products could be reduced significantly. Photoinduced isomerization reactions proceed with no change in entropy but probably cannot be used for photochemical energy storage for three reasons:

1) The thresholds (singlet-singlet transitions) are high compared with the energy stored in the high energy isomer.

2) The product is more unstable photochemically than the reactant.

3) There appears to be no way to extract the energy on demand. A bimolecular exchange reaction would also produce little entropy change and there is some evidence that internal energy may be very effective in promoting endothermic exchange reactions. A reaction (hypothetical) such as

$$NO_2 + h\nu \rightarrow NO_2*$$
$$NO_2* + M \rightarrow NO + MO$$
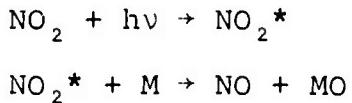
where the activation energy of the reverse thermal reaction,

$$NO + MO \rightarrow NO_2 + M$$

is at least 10 kcal/mole would be much more efficient. However no specific examples are known which appear suitable.

Finally, the utilization of differential solubility directly to create the "photochemical diode" should be possible

but in general the quantum efficiencies of dissociative processes in condensed phases is low. Photochemical redox reactions in which one product is insoluble should, however, be possible.

B.   Photogalvanic Cells

These have been studied at a leisurely pace for at least thirty years but unfortunately little quantitative information on quantum efficiencies is known. In most cases even the reaction mechanisms and charge carriers are not known with any degree of certainty. The potentials generated may be quite high, on the order of hundreds of millivolts but these apparently are open circuit voltages and the power densities and efficiencies must be investigated further.

There are at least two types of photogalvanic cells, bulk and surface. In the first the redox reaction is photochemically driven in the illuminated solution, the potential developing presumably because of the differential mobility of the species involved. In the surface mode, an electrode is coated with a thin film of dye. Illumination of the electrode in the presence of appropriate electron acceptor or donor in the solution in contact with it causes electron transfer to or from the solution to the dye, then to the electrode. Again open circuit voltages may be several hundred millivolts. The problems associated with making large electrode areas uniformly coated with appropriate dye films make this approach appear to be less promising but further research is certainly warranted.

Two examples of the cell types mentioned above are Fe^{+++} -Fe^{++}-Thionene, leucothionene and Pt electrodes coated with pthalocyanine films, respectively.

C.   Solar Energy Driven Thermochemical Processes

Although these processes are defined to be near thermo-dynamic equilibrium, apparently relatively little consideration has been given to them in relation to solar energy utilization and they deserve much more attention. Since we are considering high T processes (>300°C), we shall consider gas phase only. There appear to be several advantages in using appropriate gases directly as the solar energy absorber and as heat transfer medium if not the working fluid. These are:

a) Gases have low thermal conductivity, low total emissivity ($\geq$.2 for a .5 ft-atm layer of CO_2, H_2O, HCl, etc., and less for homonuclear diatomics).

b) Some gases (such as l_2, NO_2) have high absorption coeffic-ients in the visible region of the spectrum. These two characteristics make the "a/e" ratio of these substances on the order of 10-20 in some pressure ranges and layer thicknesses.

c) If the gas undergoes an endothermic decomposition at an appropriate temperature, the heat capacity in that temper-ature range may be increased by a reasonably large factor (3-8X). This means that smaller amounts of gas must be handled, and a larger fraction of the energy absorbed can

-162-

be evolved at a high temperature.

Consider NO_2 as an example. The absorption coefficient, α, is >1 ℓ-mole^{-1} cm^{-1} from 7000Å through the near UV; $\alpha > 10$ ℓ-mole^{-1} cm^{-1} for $\lambda < 6000$Å, and $\alpha > 100$ ℓ-mole^{-1} cm^{-1} for $\lambda < 5000$Å. Thus a 10 cm layer at 1 atm pressure will absorb $>90\%$ of the visible solar radiation, and the inherent emissivity of such a layer should be less than 0.2. At 1 atm total pressure the dissociation reaction

$$2NO_2 \rightarrow 2NO + O_2$$
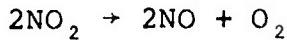
becomes important at roughly 300°C. The ΔH°_{298} for the reaction is 13.6 kcal/mole NO_2, and the equilibrium constant as a function of temperature is:

| $T(K)$	$K = \dfrac{P_{NO}^{\;2} P_{O_2}}{P_{NO_2}^{\;2}}$ atm	$\alpha = \dfrac{P_{NO}}{P_{NO_2}}$ for $P_{TOT} = 1$ atm
600	5×10^{-3}	.2
700	.15	1
800	1.8	2.6
(850)	4.9	4

The effective heat capacity of this gas between 600K and 800K at 1 atm is greater than 60 kcal/K-mole (including effects of reaction), roughly 8 times that of a diatomic gas such as N_2. At higher total pressures, of course, the temperature at which a given fraction of the gas is dissociated is increased (at 10 atm total pressure, for example, $P_{NO}/P_{NO_2} = 1$ at $\sim$790K). In

addition the photochemical reaction,

$$NO_2 + h\nu(\lambda < 4000\overset{\circ}{A}) \to NO + O$$

$$O + NO_2 \to NO + O_2$$

will increase somewhat the extent of reaction even though the
reverse termolecular recombination,

$$2NO + O_2 \to 2NO_2$$
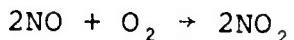
has a low activation energy and is rapid at atmospheric pressures
($k_r \sim 10^{12} e^{-1,000/RT} cm^6 mole^{-2} sec^{-1}$).

Although we do not purport to present detailed estimates
here, it seems likely that with reasonable solar concentrators
($\sim$10X) and I.R. reflecting coatings on a transparent (visible)
vacuum enclosed pipe about 10 cm in diameter containing $\sim$2 atm
NO_2, NO, O_2 would yield an economical thermal solar collector
operating efficiently ($10 \times \frac{a}{e} \simeq 50$) to produce a high energy NO_2,
NO, O_2 mixture at 500 to 600°C (800-850°K). Note, however, that
pyrex glass softens at $\sim$850K, 550°C. Such a system has the further
advantage that the working or heat transfer fluid (NO_2) is easily
stored as liquid N_2O_4 (b.p. $\sim$21°C).

With this system, unfortunately, the back reaction is so
fast and the physical properties of O_2 and NO are so similar that
separation at high temperature and storage as fuels does not seem
feasible. This may, however, be possible with other chemical
systems and should not be ignored.

In summary there appear to be two possible direct photo-
chemical routes to solar energy storage and/or utilization: low
temperature photoinduced reactions and photogalvanic cells.
Although there appear to be few such reactions known, and the
known examples are marginal in terms of efficiency (NOCl) or not
yet studied quantitatively with respect to power production, it
seems that these areas could benefit from basic and exploratory
scientific research, particularly with respect to the underlying
processes and mechanisms in photogalvanic cells. In the case of
the thermal chemical conversion by solar energy, much is known
about the basic processes but little consideration has yet been
given to the probable advantages of these systems by those most
concerned with large scale solar energy conversion. There appear
to be two possible important advantages:

1) Large "bulges" in the heat capacity in appropriate temper-
    ature ranges leading to high efficiency as thermal storage
    and transfer fluid.

2) Effective utilization of the optical properties of gases
    which may have very large inherent visible absorption to
    I.R. emission ratios.

In the above the materials problems are likely to be associated
with:

1) Handling high temperature highly reactive chemicals.

2) Finding confinement materials of appropriate inertness,
    optical properties, and strength.

3) For photogalvanic processes, those problems associated with efficient electrode materials.

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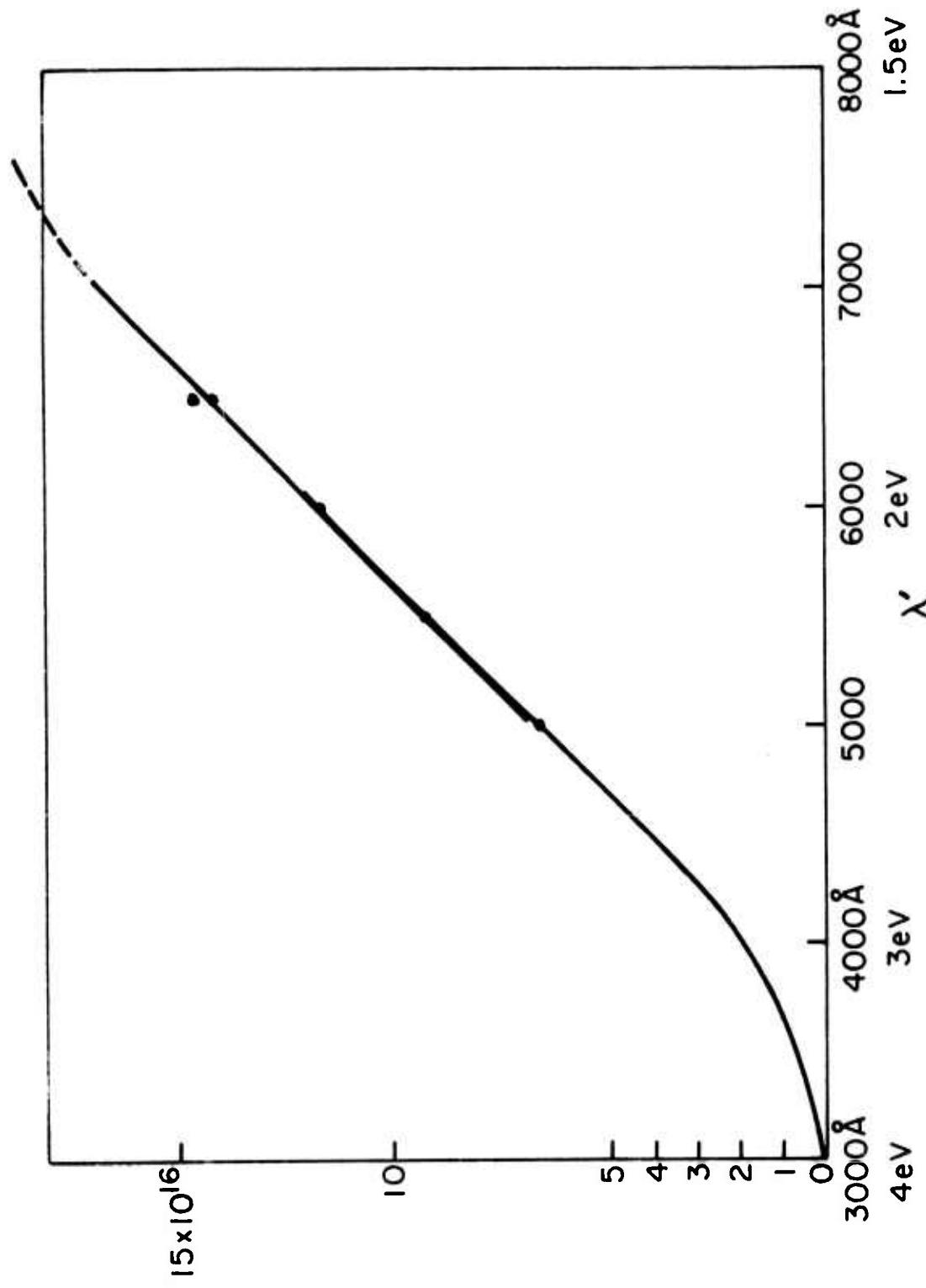
Figure 1. Number of photons per cm^2 per sec with wavelength $< \lambda'$ at earth's surface at normal incidence at equator.
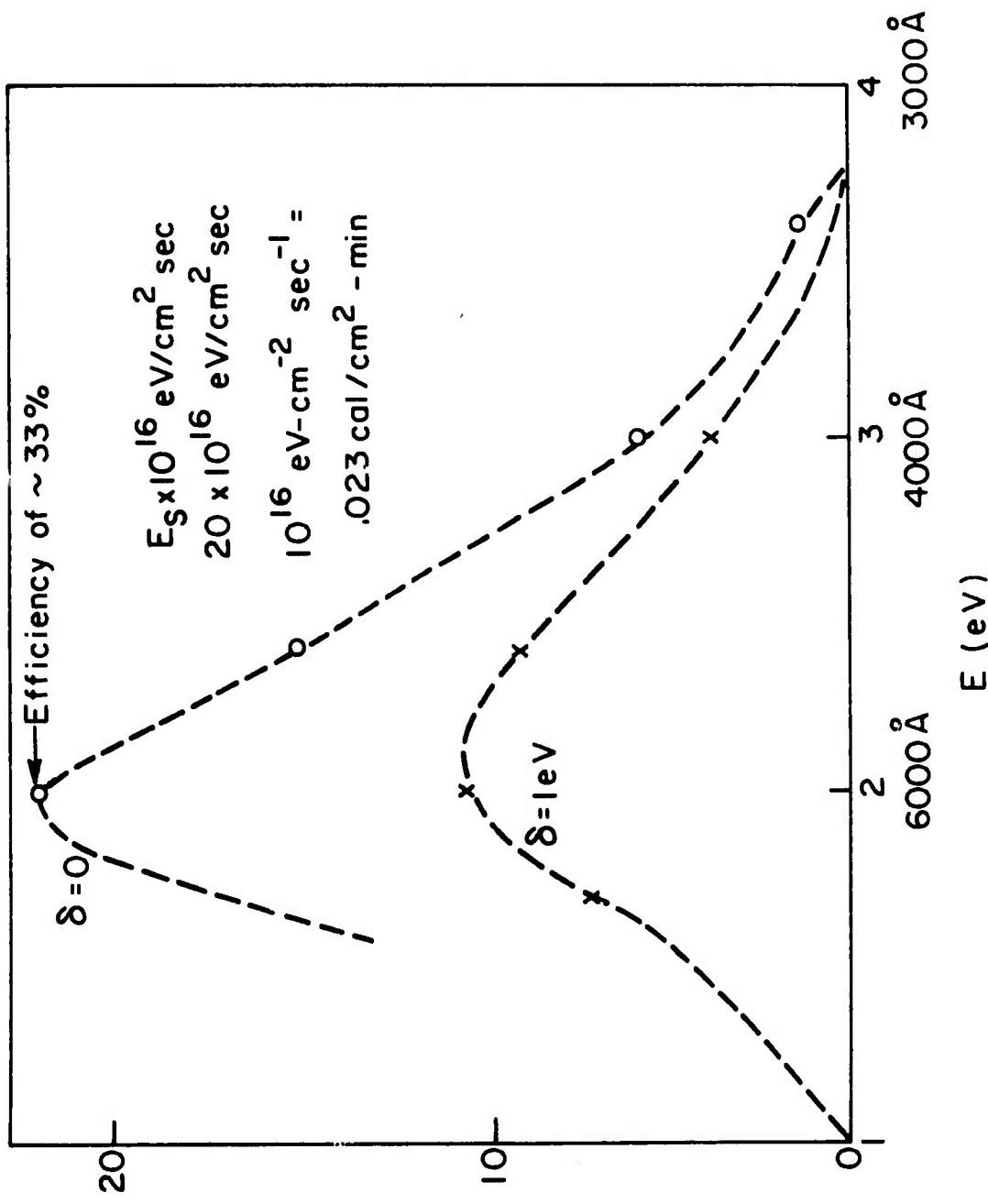
Figure 2. Efficiency of Threshold Processes: Energy stored per cm^2-sec^{-1} as a function of threshold energy and energy stored per photon. Solar spectrum of Figure 1 assumed.

PHOTOGALVANIC CELLS

R. Gomer

Abstract

An analysis of photogalvanic cells is carried out and applied to a specific system, iron-thionine, with only slight simplifications. The criteria for successful cell design are given and discussed. It is concluded that many formidable obstacles to practical application exist. The principal difficulties are the following: 1) Diffusion to the electrodes and reaction there must be sufficiently rapid to make bulk back reactions unimportant. 2) A means for keeping at least one active species from reaching one electrode must be found. 3) A sufficient range of the solar spectrum must be exploited without increasing the rate of photon absorption to the point where bulk back reaction becomes important. These problems are discussed in some detail and quantitative criteria are presented in terms of absorbed photon flux, cell size parameters, chemical rate constants, exchange current densities, overvoltages and diffusion coefficients.

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PHOTOGALVANIC CELLS

R. Gomer

The current search for additional energy sources has
drawn renewed attention to the utilization of solar energy.
Among the various schemes for its exploitation direct conver-
sion into electricity has obvious advantages, in principle.
The most widely used and developed device for this purpose is
the silicon solar cell. While sturdy and reliable, and reason-
ably efficient (12% to 15% of incident flux, with a potential
of 18%) its current cost is astronomical -- $500/watt. The
principal reason for this high cost is the necessity of using
very pure single crystals of Si. Although greater demand, and
a sacrifice in efficiency can undoubtedly lower the cost, it
seems worthwhile at least to explore the feasibility of other
approaches. This paper attempts to do this for a little known
and less understood device, the photogalvanic cell. Although
the existence of a photogalvanic effect was apparently dis-
covered in 1925[1], it was first seriously considered by
Rabinowitch[2] in 1940, who investigated the iron-thionine system.
His work has been followed in the nineteen fifties by some
attempts to devise useful cells,[3,4,5] although no serious analysis
of their operating principles has been carried out. Very briefly
the basis of a photogalvanic cell is the following. A solution

containing a light absorbing dye capable of being reduced (thionine chloride) and an ion capable of being oxidized (Fe^{+2}) is irradiated. The dye absorbs light via a singlet-singlet transition and decays rapidly to a long-lived triplet state in which it is capable of being reduced (in the case of thionine to semithionine chloride and further to leucothionine). In the absence of light the equilibrium of the reaction

$$T^+ + Fe^{+2} + H^+ \rightleftarrows TH^+ + Fe^{+3} \tag{1}$$
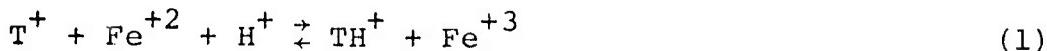
where T^+ stands for thionine ion, and TH^+ for semithionine ion lies far to the left. The effect of irradiation is thus to produce an endoenergetic state in which the Fe^{+3} and TH^+ concentrations exceed their equilibrium values. It is possible to utilize this free energy gain in a galvanic cell, if one electrode is placed in the illuminated solution while a second electrode is placed in an unilluminated compartment in contact with the former. A portion of the absorbed energy will be lost by the reaction

$$TH^+ + Fe^{+3} \rightarrow T^+ + H^+ + Fe^{+2} \tag{2}$$
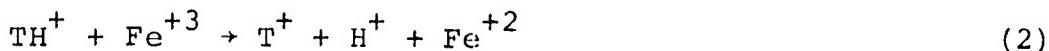
in the bulk of the solution, and also if this reaction occurs as a short circuit at one or both electrodes. These processes constitute the analogue of electron-hole recombination in a photovoltaic cell. The above seems to represent approximately the point to which the theory of photogalvanic cells has been pushed.

Before discussing photogalvanic cells in more detail a number of general points must be made. Photovoltaic cells suffer from the fact that photon energies in excess of the band gap are wasted. Nevertheless, there are bands in solids and so, beyond the threshold imposed by the gap, absorption is generally strong in direct gap materials for all wavelengths shorter than threshold. Dyes on the other hand contain a very small number of atoms and consequently have much more discrete energy spectra, so that absorption generally centers on a fairly narrow spectral region (.1 - .2 eV) around the absorption maximum. Dyes with a broader absorption range generally have lower extinction coefficients. Thus, unless mixtures of dyes, or a stack of cells containing different dyes is used, photogalvanic cells will utilize an inherently smaller fraction of the solar spectrum than photovoltaic cells, even if shortcircuiting processes could be avoided.

To some extent this drawback is counterbalanced by the fact that a reaction like (1) leads to very little entropy change, or actually a decrease, which is good from our point of view. By contrast most endoenergetic photochemical reactions which occur over a wide spectral range necessarily involve dissociation (e.g., $NOCl \rightarrow NO + \frac{1}{2}Cl_2$) and thus an entropy increase, which makes the net free energy gain much smaller than the enthaply change.

Finally some practical considerations should be mentioned at the outset. Since photogalvanic cells involve easily oxidiz-

able substances, operation requires oxygen free solutions, and thus at least minimally airtight construction which may offset the cheapness of the active ingredients. Since organic substances are less stable than silicon, there is also the problem of dye degradation. There is some evidence that this is a problem with the thionine system, but it is far from clear whether this is inherent or due to faulty technique. Since an appreciable fraction of incident radiation will be converted into heat under the best of conditions the stability problem is likely to be aggravated under actual operating conditions. Finally experiments carried out to date have used platinum electrodes, which is hardly the direction in which to go for large scale application. Inexpensive, inert electrode materials would have to be used in any operational system. We shall show that the efficient operation of a photogalvanic cell requires membranes impermeable to at least one of the photochemically produced active species, e.g., a membrane which permits passage of small inorganic ions but not of dye molecules or ions and preferably another membrane permeable only to dye species. The development of suitably thin membranes of this kind, sufficiently inert to stand up under operating conditions is only one of the serious impediments to the practical development of photogalvanic cells.

In the following we shall discuss the mechanism of a photogalvanic cell and derive expressions for voltage, current, power, and efficiency. For the sake of specificty we shall couch the discussion in terms of the thionine-iron system, but will make

a number of simplifying assumptions. Thus we shall assume that the first reduction product, semithionine, is the only species of importance, and shall ignore complications arising from the existence of leukothionine, such as the oxidation of semi-thionine, by leukothionine.

When reaction (1) occurs photochemically in a solution containing the reactant and product species at given concentrations (or properly activities) the Gibbs free energy energy increase, expressed as a voltage is given by

$$E = E^0 + \frac{RT}{F} \ln \frac{Fe^{+3} \cdot TH^+}{Fe^{+2} \cdot T^+ \cdot H^+} \tag{3}$$

where $E^0 = 0.47$ volts is found from the standard reduction potentials for $Fe^{+2} \rightarrow Fe^{+3} + e^-$; $E^0 \simeq -0.77$ volts, and the reduction potential for $TH^+ \rightarrow T^+ + H^+ + e^-$; $E^0 \simeq 0.3$ volts.[2] When an attempt is made to exploit the inverse, reaction 2 galvanically, the useful free energy change, again expressed as a voltage, is given by a similar expression, with the understanding that the concentrations of T^+ and TH^+ refer to the illuminated (negative) electrode and those of Fe^{+2} and Fe^{+3} to the dark (positive) electrode:

$$E = E^0 + \frac{RT}{F} \ln \left[\left(\frac{Fe^{+3}}{Fe^{+2}} \right)_D \left(\frac{TH^+}{TH^+ \cdot H^+} \right)_L \right] \tag{4}$$

where the subscripts refer to concentrations at L(ight) and D(ark) electrodes. The reason for this is that the only net reaction which leads to no other change than the conversion of

photon into electrical energy, i.e., which is the only one which
can occur once steady state is reached is the inverse of (1),
as indicated in Fig. 1. It is possible of course to achieve the
same overall results differently, for instance by the reduction
of T^+ at the positive electrode to TH^+, which is in turn reduced
by Fe^{+3} diffusing into the dark compartment from the illuminated
one. However, we must seek systems for which the bulk phase
reactions are slow and hence mechanisms of this kind will be
ignored. (They affect in any case only the kinetics and hence
the actual concentrations of the reacting species, but not the
validity of Eq. (2).)

As pictured in Fig. 1 we must then consider the following
(1) creation of TH^+ and Fe^{+3} in the illuminated bulk solution
(2) diffusion of these species to the electrodes
(3) reaction at the electrodes
(4) bulk recombination to Fe^{+2} and T^+
Although it is quite obvious from this simple picture, it has
apparently not been appreciated that very little electrical
energy will be obtained if both TH^+ and Fe^{+3} can diffuse rapidly
to both electrodes, even if one electrode is unilluminated, but
that it is essential that TH^+ diffuse easily to one electrode
and Fe^{+3} to the other. Faulty appreciation of this point may
have been responsible for the minute currents and efficiencies
obtained by previous designs.

The first step in obtaining an expression for voltage and current is to determine the steady state concentrations of the active species at the electrodes and in the bulk; we employ the following terms for a given species:

c_e^L concentration at L(ighted) electrode

c_s concentration in S(olution)

c_e^D concentration at D(ark) electrode

I incident absorbed photon flux in Einstein/cm^2/sec

       (1 Einstein = 6.02×10^{23} photons)

q quantum yield

k^L rate constant for the disappearance of a species at electrode L

k^D rate constant for disappearance of a species at electrode D

To conform to past usage we continue to call the electrode which can be freely reached by TH$^+$ the L(ighted) electrode and the one at which Fe^{+3} → Fe^{+2} is the only reaction D(ark) electrode, although a reasonable cell design would distinguish these only by the fact that a membrane impermeable to TH$^+$ is placed in front of the electrode D. In the following analysis we will also assume that the absorbed light intensity is uniform not only in the direction perpendicular to the incident light, but also parallel to it, i.e., that there is no variation in absorbed intensity with depth in the cell. This is clearly incorrect unless the extinction coefficient is small, or a different

-178-

arrangement from that of Fig. 1 is used, in which the light enters perpendicularly to an electrode, for instance by making one electrode from conductivized glass, and allowing the light to enter through it.

We then have at steady state at an electrode

$$-dc_e/dt = k\,c_e \tag{5}$$

which corresponds to a current i

$$i = k\,\lambda\,A_e F\,c_e \tag{6}$$

where F is the Faraday ($\sim$95,000 coulombs/mole), A_e the electrode area and λ a distance, of the order of $2 - 3\text{\AA}$, which corresponds to the actual transition distance which an ion being charged or discharged moves in the process of being (dis)charged. The amount diffusing into the region immediately in front of the electrode is, in # of moles (or molecules)

$$\# = A_e\,D\,dc/dx \simeq A_e\,(D/x_1)c_s - c_e) \tag{7}$$

where x_1 is the approximate width of the illuminated bulk solution, and D is the relevant diffusion coefficient. This leads to a concentration change at the electrode

$$+dc_e/dt = (D/\lambda x_1)\,(c_s - c_e) = (a/\tau)\,(c_s - c_e) \tag{8}$$

where

$$a = x_1/\lambda \tag{9}$$

and

$$1/\tau = D/x_1^2 \tag{10}$$

At steady state we thus have

$$c_e = c_s \frac{a/\tau}{k+a/\tau} \tag{11}$$

In the bulk of the solution the average concentration change induced by photon absorption is the result of a quasi-unimolecular reaction, that is at sufficiently high Fe^{+2} concentrations it will be simply

$$dc_s/dt = q\, I/x_2 = Q \tag{12}$$

where x_2 is the depth of the cell.

It is possible of course to include the Fe^{+2} and H^+ concentration in q.

Thus, at steady state in solution we have for species (1), TH^+,

$$\left(\frac{1}{\tau_1^L}\right)\left(c_{s1}-c_{e1}^L\right)+\left(\frac{1}{\tau_1^D}\right)\left(c_{s1}-c_{e1}^D\right) + k_R c_{s1} c_{s2} = Q \tag{13}$$

with an analogous equation for species 2 (Fe^{+3}). The τ are defined by Eq. (10) but account is taken of the possibility of changing the diffusion coefficients at the light and dark electrodes by the introduction of membranes. k_r is the rate constant of the bulk reaction (2). Combination of Eqs. (11) and (13) leads to expressions for the concentration c_s:

$$c_{s1} = -\alpha_2/k_r + \sqrt{(\alpha_2/k_r)^2 + \frac{Q}{k_r}(\alpha_2/\alpha_1)} \qquad (14a)$$

$$c_{s2} = -\alpha_1/k_r + \sqrt{(\alpha_1/k_r)^2 + \frac{Q}{k_r}(\alpha_1/\alpha_2)}$$

where

$$\alpha_1 = \frac{k_1^L}{k_1^L \tau_1^L + a} + \frac{k_1^D}{k_1^D \tau_1^D + a} \qquad (15)$$

with a similar expression for α_2.

Several limiting cases deserve attention

I.   Bulk Recombination dominates, $\alpha_1 \alpha_2 \ll k_r Q$

In this case, of little practical interest since most of the photon energy is wasted

$$c_{s1} = \sqrt{\frac{Q}{k_r}(\alpha_2/\alpha_1)^2} \qquad (16)$$

$$c_{e1}^L = \frac{a/\tau_1^L}{k_1^L + a/\tau_1^L} \, c_{s1} \qquad (17)$$

$$c_{s2} = \sqrt{\frac{Q}{k_r}(\alpha_1/\alpha_2)} \qquad (18)$$

and so on. If diffusion is rapid, relative to reaction at the electrode, i.e., if $\alpha_i/\tau_i \gg k_i$

$$c_{e1} \rightarrow \sqrt{\frac{Q}{k_r}(\alpha_2/\alpha_1)} \simeq \sqrt{\frac{Q}{k_r}} \qquad (19)$$

$$c_{e2} \rightarrow \sqrt{\frac{Q}{k_r}(\alpha_1/\alpha_2)} \simeq \sqrt{\frac{Q}{k_r}} \qquad (20)$$

-181-

If diffusion is slow, i.e., if $\alpha/\tau_i \ll k_i$,

$$c_{e1} \rightarrow \frac{a/\tau_1}{k_1} \sqrt{\frac{Q}{k_r}(\alpha_2/\alpha_1)} \tag{21a}$$

$$c_{e2} = \frac{a/\tau_2}{k_2} \sqrt{\frac{Q}{k_r}(\alpha_1/\alpha_2)} \tag{21b}$$

Thus, if diffusion is rapid relative to electrode reaction, concentrations at the electrode are determined entirely by $I^{\frac{1}{2}}$ and the cell emf takes the extremely simple form*

$$E = E^0 + \frac{RT}{F} \ln \left(\frac{qI \times 10^6}{k_r x_2 Fe^{+2} \cdot T^+ \cdot H^+} \right) \tag{22}$$

provided that Fe^{+3} is kept from the L electrode or TH^+ from the D electrode. If reaction rates at the electrodes dominate over diffusion

$$E = E^0 + \frac{RT}{F} \ln \left[\frac{qI \, a^2 \times 10^6}{k_r x_2 \tau_1 \tau_2 k_1^L k_2^D \, Fe^{+2} \, H^+} \right] \tag{23}$$

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*The factor 10^6 in the logarithmic term for the emf arises as follows. All concentrations calculated from our steady state assumption have been expressed in moles/cm^3. Since the E^0 values are based on concentrations expressed in moles/liter, we must convert the concentrations of TH^+ and Fe^{+3} to these units. If k_R is expressed in units of (moles/liter)$^{-1}$sec^{-1} rather than in units of (moles/cm^3)$^{-1}$sec^{-1} as implied in our formulas the factor 10^6 must be replaced by 10^3.

II. Bulk Recombination Unimportant, $\alpha_1 \alpha_2 >> k_r Q$

In this case, which is the situation which must be achieved
in any useful device inspection of Eq. 13 or expansion of the
square root in Eq. (14) shows that

$$c_e^L = \frac{(qI/\lambda)(x_1/x_2)}{k^L \tau^L + a} \cdot \left[\frac{k^L}{k^L \tau^L + a} + \frac{k^D}{k^D \tau^D + a} \right]^{-1}$$

$$= \frac{qI}{\lambda} \frac{(x_1/x_2)}{k^L + k^D \left(\frac{k^L \tau^L + a}{k^D \tau^D + a} \right)} \qquad (24)$$

with analogous expressions for c_e^D. The subscripts 1, 2 have
been omitted, since Eq. (24) holds for both TH^+ and Fe^{+3}. If
$\tau^L \simeq \tau^D$, $k^L \simeq k^D$ it is clear that concentrations of a given
species at both electrodes will be nearly equal so that no
appreciable energy can be drawn from the cell. We therefore
continue assuming that at least one reactive species, TH^+ (being
the bigger ion) can be kept from reaching electrode D by a
suitable barrier, so that $\tau_{TH^+}^D \to \infty$.

In order to simplify the following expressions slightly
we also assume that $\tau_{Fe^{+3}}^L \simeq \tau_{Fe^{+3}}^D$, although this is clearly not
necessary, or in the presence of a membrane, likely to be the
case. We have for TH^+ at electrode L

$$c_{e_1}^L = \frac{qI(x_1/x_2)10^3}{\lambda k_1^L} \qquad \text{moles/liter} \qquad (25)$$

This relation is entirely independent of the relative magnitudes
of k_1^L and a/τ^L. In the case of Fe^{+3} however we must distinguish
between rapid diffusion, relative to electrode reaction and the
inverse. Assuming first that diffusion is slow, i.e., $k >> a/\tau^D$

-183-

$$c_{e2}^{L} = \frac{qI(x_1/x_2)10^3}{\lambda k_2^{L}(1+\tau_2^{L}/\tau_2^{D})} \qquad \text{moles/liter} \qquad (26)$$

$$c_{e2}^{D} = \frac{qI(x_1/x_2)10^3}{\lambda k_2^{D}(1+\tau_2^{D}/\tau_2^{L})} \qquad (27)$$

If τ_{Fe+3}^{L} could be made infinite, expressions for the Fe^{+3} con-
centrations analogous to those for TH+ would result, i.e., they
would not contain diffusion coefficients. If $\tau_{Fe+3}^{D} \simeq \tau_{Fe+3}^{L}$
this would be equally true, with the appearance of an extra
factor of $1/2$ in the Fe^{+3} concentrations.

If diffusion is rapid relative to electrode reactions,
i.e., if $k \ll a/\tau$

$$c_{e2}^{D} = c_{e2}^{L} = (qI/\lambda)\frac{(x_1/x_2)\times10^3}{k_2^{L} + k_2^{D}} \qquad (28)$$

Finally if diffusion to the dark electrode D is slow, because
of a membrane, but rapid to the light electrode we find

$$c_{e2}^{L} = \frac{(qI/\lambda)(x_1/x_2)10^3}{k_2^{L} + a/\tau_2^{D}} \qquad (28)$$

$$c_{e2}^{D} = \frac{(qI/\lambda)(x_1/x_2)10^3}{k_2^{D}[1+k_2^{L}(\frac{\tau_2^{D}}{a})]} \qquad (29)$$

We are now able to write expressions for the cell emf
by substituting the expressions for the concentrations of
relevant species in Eq. (4). In order to simplify matters
slightly we shall only write an explicit expression for the
case that diffusion is slow, relative to electrode reaction,

which is probably realistic in any case. We then have

$$E = E^0 + \frac{RT}{F} \ln \left\{ \frac{(qI/\lambda)^2 (x_1/x_2)^2 10^6}{k_1^L k_2^D n \; Fe^{+2} \; T^+ \; H^+} \right\} \tag{30}$$

Here $n = 1 + \tau_2^D/\tau_2^L$ and the subscripts 1 and 2 stand for TH^+, and Fe^{+3}, respectively.

As it stands Eq. (30) is incomplete, since electrochemical rate constants depend on emf, and we will have to go further. However even in its present form the expression for cell emf is interesting. First emf depends on the square of absorbed light intensity. Second the slower the rate constants of electrode reaction the higher the emf. This comes about of course from the fact that the higher the concentrations of TH^+ and Fe^{+3} achievable, the higher the emf; if no other factors intervened this would be achieved by minimizing electrode reaction constants. It must be remembered of course, that the regime of validity of Eq. (30) is based on the assumption that bulk recombination is unimportant, so that in fact there is no way of driving up the concentrations at the electrode beyond the limits set by this requirement.

Before continuing the discussion of cell emf it is useful to write expressions for the current. The current flowing in the external circuit is determined by the rate of Fe^{+3} reduction at electrode D:

$$i = k_2^D \lambda A_e F \; c_{e2}^D = \frac{qI A_e (x_1/x_2) F}{1 + \tau_2^D/\tau_2^L} = \frac{qI A_2 F}{1 + \tau_1^D/\tau_1^L} \tag{31}$$

-185-

where A_2 is the area of the cell normal to the direction of photon incidence. The (wasteful) shortcircuit current at electrode L caused by the reaction of Fe^{+3} with TH^+ at that electrode is given by

$$i_s = \frac{qIFA_2}{1+\tau_2^L/\tau_2^D} \tag{32}$$

and the sum of these currents adds up to qIA_2F as it should, since we have postulated the bulk reverse reaction to be negligible.

Thus a photogalvanic cell, at given illumination will find its own current and voltage. If no external current is drawn, both the bulk reaction, and the shortcircuiting electrode reaction at D will see to it that a new steady state is reached.

If the shortcircuiting reaction at D could be eliminated entirely, the useful current would increase to qIA_eF. There is in fact a way of doing this: If the electrode L is covered with a thin layer of an intrinsic semiconductor such that the conduction band of the latter remains above the Fermi level of the electrode by an amount Δ, D will continue to be a good electron acceptor, but a poor donor. Consequently, the reaction

$$TH^+ \rightarrow T^+ + H^+ + e^- \tag{33}$$

will proceed unaltered, while the reaction rate constant for

$$Fe^{+3} + e^- \rightarrow Fe^{+2} \tag{34}$$

will be decreased by a factor of exp-(Δ/RT). Particularly if diffusion is very rapid this may be worthwhile. Of course we pay a corresponding price: In passing from the conduction band of the semiconductor to the metal, i.e., in traversing the rectifying junction, electrons lose an amount of energy Δ which is lost to us, so that the effective cell voltage has been decreased by this amount. Since $\Delta = 0.1$ eV would cause a drop of 40 in k, a worthwhile gain in E.i may result, assuming that the coating can be done cheaply.

At this point it is useful to examine the criterion for negligible bulk reaction more closely. In the most favorable case, i.e., membranes both at L and D the condition reduces to

$$\frac{k_1/\tau_1}{k_1+a/\tau_1} \cdot \frac{k_2/\tau_2}{k_2+a/\tau_2} >> \frac{qI}{x_2} k_r \qquad (35)$$

If $k > a/\tau$ for both reactions this reduces to

$$\frac{1}{\tau_1} \cdot \frac{1}{\tau_2} >> \frac{qIk_r}{x_2} \qquad (36a)$$

If $k < \alpha/\tau$ we get

$$\lambda_2\lambda_1 k_1^L k_2^D >> (x_1^2/x_2)qIk_r \qquad (36b)$$

Thus, in fact both inequalities (35b) and (36b) must be obeyed for the bulk reaction to be unimportant; these conditions can also be taken as rough criteria in the less idealized case where α_2 at least is more complicated.

We return now to evaluating the cell emf in terms of measurable or calculable qualities, i.e., we must find expressions for the electrochemical rate constants k_2^D and k_1^L. This can be done in terms of the respective exchange current densities. We have for an oxidation reaction

$$R_{(1)} \rightarrow O_{(1)} + e^-$$ (37)
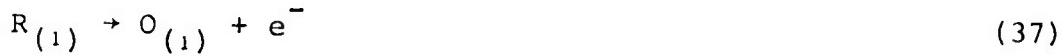
$$k_1 \lambda = \lambda k_1' e^{(1-\beta_1)(\phi_m-\phi_s)F/RT}$$ (38)

where k_1' is a "chemical" rate constant, $\phi_m-\phi_s$ the potential difference between metal electrode and solution, and β a symmetry factor, $\beta \simeq .5$. If we introduce an overvoltage η taken as a positive quantity by

$$\phi_m-\phi_s = (\phi_m-\phi_s)_e + \eta_1$$ (39)

where the subscript refers to the equilibrium potential difference, we can write

$$k_1 \lambda = \lambda k_1' e^{(1-\beta_1)(\phi_m-\phi_s)_e F/RT} \cdot e^{(1-\beta_1)\eta_1 F/RT}$$ (40)

The exchange current density, i_o is defined as

$$\frac{i_o}{FC_{O_{(1)}}} = \lambda k_1^1 e^{(1-\beta_1)(\phi_m-\phi_s)_e F/RT} \qquad \begin{array}{l} \text{ampere/cm}^2 \\ \text{per mole/liter} \end{array}$$ (41)

for a <u>given</u> $(\phi_m-\phi_s)_e$. Since we do not know the actual concentrations at the electrode in the photogalvanic cell, we must

transform i_O into an expression at standard (unit) concentrations of oxidized and reduced species, i.e., we must write

$$(\phi_m - \phi_s)_e = (\phi_m - \phi_s)_e^O + \frac{RT}{F} \ln(O_{(1)}/R_{(1)}) \tag{42}$$

where the superscript refers to the standard state P.D., i.e., when all concentrations (better activities) have unit value. Thus if we call the standard state exchange current density $i_O^O = j^O$ for short we have, by combining Eqs. (39), (41) and (42)

$$k_1\lambda_1 = \frac{j_1^0}{F} (O_{(1)}/R_{(1)})^{1-\beta_1} e^{(1-\beta_1)\eta_1 F/RT} \tag{43}$$

Similarly, for the reaction

$$e^- + O_{(2)} \rightarrow R_{(2)} \tag{44}$$

we obtain

$$k_2\lambda_2 = \frac{j_2^0}{F} (O_{(2)}/R_{(2)})^{-\beta_2} e^{\beta\eta_2 F/RT} \tag{45}$$

where β_2 and η_2 are the relevant symmetry factor and overvoltage for reaction (44) involving species (2).

Returning to the specific case at hand, where (1) stands for TH^+ we combine Eq. (25) with Eq. (43) and obtain

$$\ln\left(\frac{TH^+}{T^+ \cdot H^+}\right) = \frac{1}{\beta_1} \ln\left(\frac{qI(x_1/x_2)10^3}{T^+ \cdot H^+}\right) - \frac{1}{\beta_1} \ln(j_1^0/F)$$

$$- \frac{1-\beta_1}{\beta_1} F\eta_1/RT \tag{46}$$

Similarly, we find

$$\ln\left(\frac{Fe^{+3}}{Fe^{+2}}\right) = \frac{1}{1-\beta_2}\ \ln\left(\frac{qI(x_1/x_2)10^3}{nFe^{+2}}\right) - \frac{1}{1-\beta_2}\ \ln\left(j_2^0/F\right)$$

$$- \frac{\beta_2}{1-\beta_2}\ F\eta_2/RT \tag{47}$$

We can now combine these expressions according to Eq. (4) to obtain the cell emf; to be correct we should subtract $(\eta_1+\eta_2)$ from the emf to obtain the actual useful voltage. When this is done we obtain

$$E = E^0 + \frac{RT}{F}\left[\ln\left(\frac{qI(x_1/x_2)10^3}{T^+\cdot H^+}\right)^{1/\beta_1} + \ln\left(\frac{qI(x_1/x_2)10^3}{nFe^{+2}}\right)^{\frac{1}{1-\beta_2}}\right]$$

$$- \frac{RT}{F\beta_1}\ \ln\left(j_1^0/F\right) - \frac{RT}{F(1-\beta_2)}\ \ln\left(j_2^0/F\right) - \frac{1}{\beta_1}\eta_1 - \frac{1}{(1-\beta_2)}\ \eta_2 \tag{48}$$

The problem is thus formally solved since we can obtain j_1^0 for the semithionine oxidation and j_2^0 for the Fe^{+3} reduction as well as the respective overvoltages η_1 and η_2 experimentally by standard methods. It should be noted however that η_1 must be calculated on the basis of $i + i_s$. That is the shortcircuiting current has an effect on the overall cell potential through its effect on η_1.

We are also able now to express criterion (36b) for the unimportance of bulk back reaction in terms of measurable quantities. Some algebra along the lines leading to Eqs. (46) and (47) then shows that criterion (36b) becomes

$$\left(\frac{1-\beta_1}{\beta_1}\right)\frac{\eta_1 F}{RT} + \left(\frac{\beta_2}{1-\beta_2}\right)\frac{\eta_2 F}{RT} + \frac{1}{\beta_1}\,\ell n\left[j_1^0/F\right] + \frac{1}{\beta_2}\,\ell n\left[j_2^0/F\right]$$

$$> \left[1 + \frac{1-\beta_1}{\beta_1} + \frac{\beta_2}{1-\beta_2}\right]\ell n\left[qI\,(x_1/x_2)10^3\right] + \ell n(k_r/x_2) \qquad (49)$$

$$+ \left(\frac{1-\beta_1}{\beta_1}\right)\ell n\left(\frac{1}{T^+\cdot H^+}\right) + \frac{\beta_2}{1-\beta_2}\,\ell n\left(\frac{1}{nFe^{+2}}\right)$$

Numerical Estimates

Although an accurate estimation of possible voltage and power outputs would require specific values of I, k_R, and exchange current densities and overvoltages a rough calculation based on order of magnitude estimates of these quantities is worthwhile. We use the following values $Iq = 10^{16}$ photons/cm^2/sec in an energy range 0.2 eV at 2 eV (the rough center of thionine absorption)

$k_R = ?$

$j_1^0 = j_2^0 = 1$ ampere/cm^2/(mole/liter)

$\eta_1 = \eta_2 = 0$

$\beta_1 = \beta_2 = 0.5$

$n = 2$

$D_1 = D_2 = 10^{-5}$ cm^2/sec

$x_1 = 1$ cm

$x_1 = ?$

$T^+ = 10^{-2}$ mole/l

$H^+ = 10^{-2}$ mole/l

$Fe^{+2} = 10^{-2}$ mole/l

We inquire first into criterion (36a), namely that diffusion to the electrodes to be sufficiently rapid to make bulk reaction unimportant. With the numbers used this becomes

$$x_1^4 \, k_R \ll 6.10^{-3} \tag{50}$$

Since the constant k_R for the thionine oxidation in solution seems to be of the order of 10^6 $(mole/cm^3)^{-1}$ sec^{-1} this requirement places a severe restriction on x_1 which would have to be 10^{-3} cm. In any case we see that a practical cell would have to be constructed in accordance with criterion (36a) or (50). Thus we see at once that the first requirement of a practical cell would be to find a system with a very slow recombination rate constant k_R. Ideally 10^2 $(mole/cm^3)^{-1}$ sec^{-1} or less would be required to keep x_1 reasonable.

We examine next criterion (36b), namely adequate rapidity of the electrode reactions. Expressed in measurable quantities by inequality (48) this becomes

$$-5 \overset{?}{>} -14.3 + \log_{10} k_R x_1^3 + \log_{10} \frac{1}{T^+ \cdot H^+ \, Fe^{+2}} \tag{51}$$

If $k_r \sim 10^6$ $(mole/cm^3)^{-1}$ sec^{-1}, $x_1 = .1$ cm, $T^+ \cdot H^+ \cdot Fe^{+2}$ must exceed $\sim 10^{-6}$ $(mole/liter)^3$.

We can next estimate the cell emf from Eq. (48) using $E^0 = 0.47$ v and $x_1 = .1$ cm, $Fe^{+2} = T^+ = H^+ = 10^{-2}$ mole/l. The result if $E = 1.21$ volts. Had we used $x_1 = 0.01$ cm in order to satisfy the diffusion criterion more adequately, the emf would have decreased by 0.24 volt.

Finally the external current, from Eq. (31) turns out to be 8×10^{-4} ampere/cm^2 of useful solution surface. The preceding discussion has indicated that a sensible cell design requires electrodes with active surfaces parallel to the incident light flux vector. Thus the effective area receiving photons must be corrected for the electrode and membrane edge areas. This introduces an additional inefficiency factor $\gamma = 1-nt$ where n is the number of electrodes/cm and t the thickness of electrode plus membrane. Probably $\gamma = 0.8$ to 0.5. Thus the power generated by our idealized cell will be 0.5γ milliwatt/cm^2 of exposed surface. The efficiency in terms of active photons absorbed (assuming a photon energy of 2 eV) is thus 0.25γ $(1.2/2) = 30\gamma\%$. The efficiency in terms of the total solar energy flux, ~ 0.1 watt/cm^2, is much less of course, being $1.0\gamma\%$.

Conclusions

The foregoing analysis indicates that photogalvanic cells may hold some promise for solar energy production provided systems can be found which conform to the following rather stringent conditions:

(1) the rate constant of bulk back reaction must be small, preferably 10^2 (mole/cm^3)$^{-1}$ sec^{-1}, unless electrode spacings of 10^{-2} cm or less prove feasible. The combined electrode and membrane thicknesses must be so small that the waste factor due to uselessly illuminated area is small.

-193-

(2) Exchange current densities of the order of 0.1 to 1 amperes/ cm^2 per mole/liter are required for the electrode reactions

(3) A means of preventing at least one of the active species from reaching one electrode must be found; it would also be useful to prevent shortcircuiting reactions at the electrode not surrounded by a membrane.

(4) A means of making $qI/x_2 \lesssim 10^{16}$ photons/cm^3/sec must be found, which nevertheless permits utilizing a much wider range of the solar spectrum. This would require either stacks of photogalvanic cells, containing different solutions, absorbing in differing spectral ranges, in such a way that light transmitted by the first cell passes into the next, and so on, or a single cell containing a substance absorbing relatively weakly, but over a wide spectral range. For such a cell x_2 would have to be made appropriately large.

(5) Electrodes, membranes, and electrolytes would have to be stable over long periods of time. The problems of devising relatively cheap stable electrode materials and membranes may be considerable. Similarly it may be difficult to devise suitable organic light absorbers which show the requisite stability. It may be considerably easier to think of inorganic redox systems which are stable, but in that case careful attention would have to be paid to the problem of a differentiating membrane because of the comparable sizes of inorganic ions. It may be possible to devise a chelate system which is both stable and contains one species of sufficient size to make membrane separation feasible.

In summary the problems facing the practical exploitation of solar energy through photogalvanic cells are many and formidable. If nothing else, the analysis presented here makes it possible to see what these problems are, and what the quantitative criteria for a successful cell would have to be.

Acknowledgement

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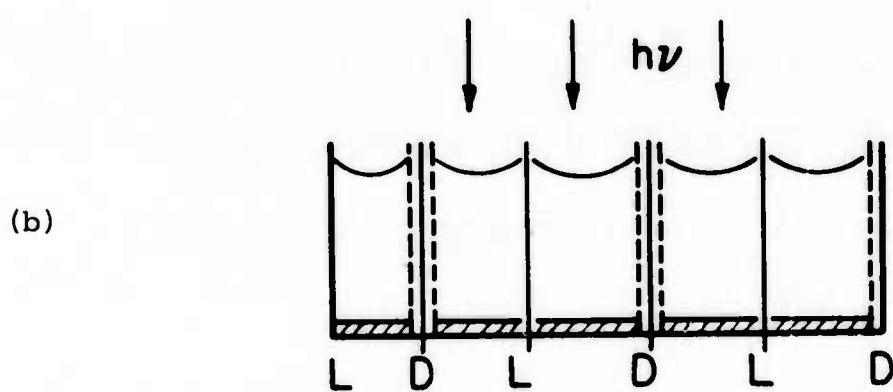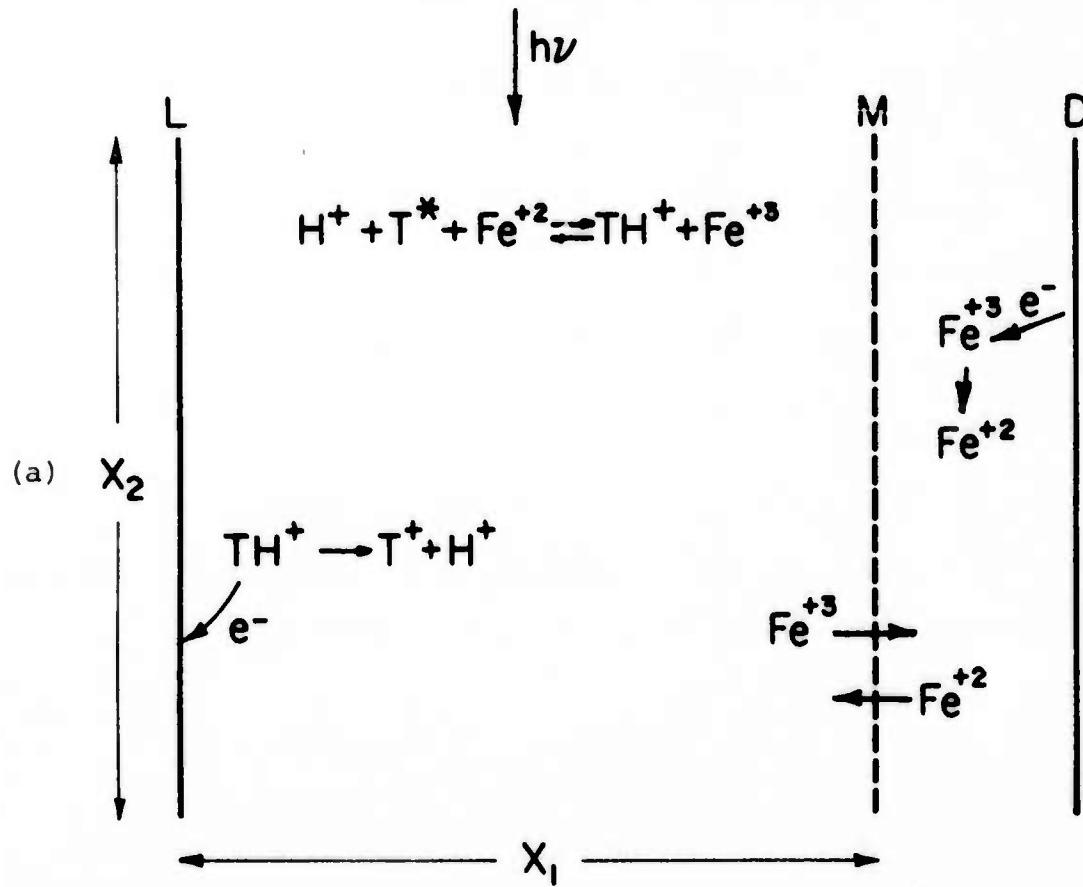
Figure 1a. Schematic diagram of a photogalvanic cell employing the thionine-iron system. L negative, D positive electrode; M, membrane impermeable to TH^+ (semithionine ion) but permeable to Fe^{+3} and Fe^{+2} ions. x_1 width of cell, x_2 depth of cell.

b. Schematic arrangement for a photogalvanic battery.

-196-

APPARATUS FOR CONVERTING SOLAR ENERGY
INTO ELECTRICITY*

G. A. Korsunovski

As translated by Richard Gomer

Declared May 3, 1961, as No. 728983/26 in the Bureau
for giving testimony of inventions for the Council of Ministers
of the USSR.

Published in "Bulletin of Inventions" No. 20 for 1962.

The new apparatus for converting solar energy to electri-
city consists of a photogalvanic cell using a photo-reducible dye,
a reducing agent and a photo-catalyst.

The distinctive, special feature of the photoelectric
apparatus is the combination of dye (thiazine), reducing agent
(water) and photocatalyst (zinc oxide and titanium dioxide in
powder form). In the above mentioned application the photo-
catalyst increases the conversion efficiency of the device.

The schematic diagram describes the apparatus: A layer
of semiconductor (6), acting as photocatalyst is placed in the
communicating vessels (1) and (2) which are made of insulating
material, preferably glass or plastic with bottoms (3) and (4)

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*No. 150885, "Description of an Invention from the Author's
Testimony, Associated with Group No. 89.

of conducting glass, filled with solution (5) of oxidizing agent. As oxidizer one should use thiazine or oxazine dye in a water solvent acting as reducing agent; the photocatalyst is zinc oxide and titanium dioxide in powder form. The solution and space above it are deoxygenated by means of the outlet duct (7) with a pump, (not shown on diagram) or by flowing nitrogen. Under one of the vessels is installed a mirror (8).

When sunlight enters vessel (2) through the conductive glass by means of mirror (8), a photoreduction of the dye into a leuco-form occurs; simultaneously water is photo-oxidized into hydrogen peroxide.

On account of the difference in concentrations of the leuco-dye at the illuminated and unilluminated electrodes a difference in potential arises. The cell generates electric current to equalize the concentration of the leuco-form at the electrodes.

For continuous illumination a potential difference would be maintained at the electrodes.

Object of the Invention

The apparatus for converting solar energy into electricity consists of a photogalvanic cell containing a photoreducible dye, a reducing agent and a photocatalyst to increase the conversion efficiency.

It uses thiazine as the dye, water as the reducing agent and zinc oxide and titanium dioxide in powder form as the photo-catalyst.
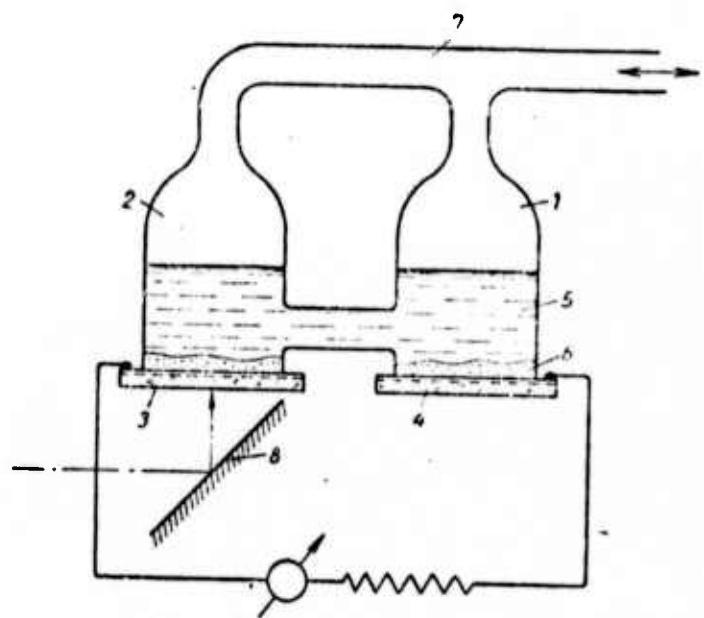
SOLAR SEA POWER

C. Zener

1. INTRODUCTION

Solar energy will be used to generate a significant amount
of electric power only when such generation becomes economically
feasible. Because of the low energy concentration of sunlight,
the capital cost of the equipment to collect and concentrate solar
radiation presents a major obstacle to economic feasibility. In
order to obtain a feeling for this economical obstacle we calculate
the average power generated by the radiation falling upon one
square foot of the earth's surface, the thermal energy to electric
power conversion being assumed to occur at a typical efficiency
of 20%. This power is 0.01 kilowatt. Since the capital cost of
a nuclear power station is ∿$500/kw, economic feasibility implies
a collector cost small compared to $5/ft^2. This collector cost
can, however, be completely circumvented by making use of the
collector which nature has provided us--namely the oceans.

Heat engines must be provided not only with a heat source
but also with a mechanism for receiving the rejected heat. This
mechanism is commonly call a heat sink. Adequate heat sinks pre-
sent an increasingly difficult problem in conventional power plants.
In fact, the heat sink problem is a major factor in the trend to

-201-

push further nuclear power plants off the continental USA into the adjoining ocean. Adequate heat sinks present an even more difficult problem for projected solar power plants in the arid regions of the Southwest. Fortunately, if we make use of the heat collector that nature has given us, we automatically have the solution to our problem of a heat sink.

A power plant which uses the ocean as both a collector of solar energy and a heat sink we call a solar sea power plant (SSPP). The essential features of such a plant are presented in Figure 1.
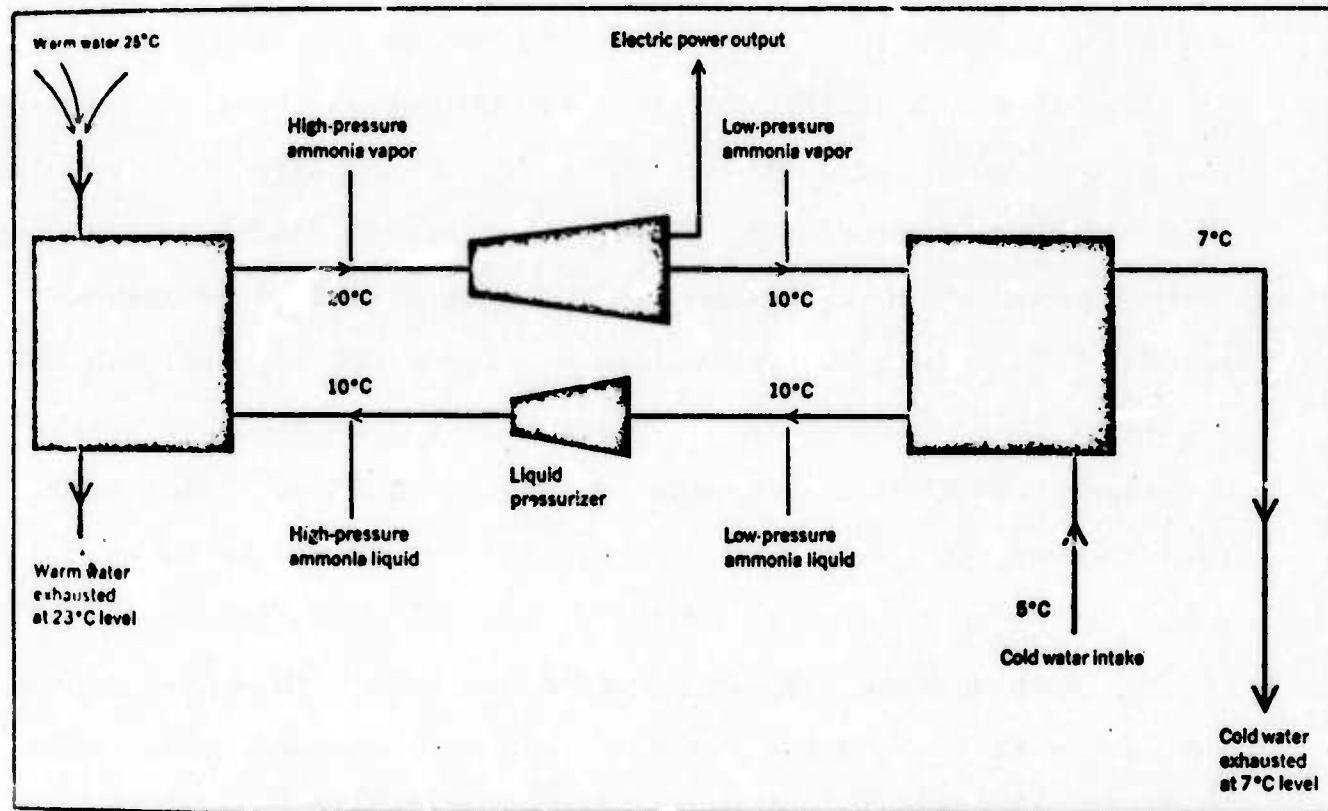
Schematic diagram of a solar sea power plant. Ammonia is assumed to be the working fluid in the boiler, turbine and compressor in this example, but more recently developed refrigerating fluids, such as the freons, might be preferable. The quantity of water passing through the boiler is comparable with that passing through a hydroelectric plant with the same output.

Figure 1. Source: C. Zener, "Solar Sea Power," <u>Physics Today</u>, January 1973, page 50.

A SSP is located at the top of the ocean thermocline.
A typical sample of a thermocline in the tropical ocean is
illustrated in Figure 2.
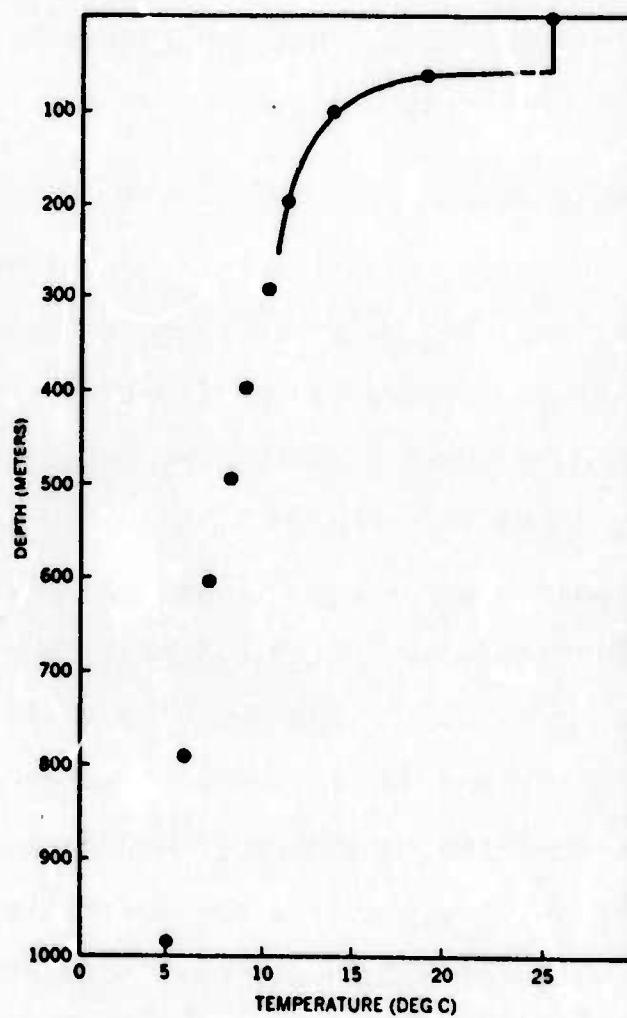
Typical temperature profile in the tropical ocean, taken from F.C.
Fuglister (reference 8, pages 119 and 186).   The black dots are
readings at 8°22'N, 27°27'W, and the solid curve is a continuous
recording at 8°24'N. 27°27'W.

Figure 2.   Source: C. Zener, "Solar Sea Power," Physics Today,
          January 1973, page 52.

-203-

The sharp upper boundary of the thermocline arises basically from the essential incompatibility of turbulence and of thermal (or density) stratification. Since turbulence is introduced by the action of the wind, and since a temperature difference does exist between the top and bottom of the ocean, the ocean must separate into two phases, one with turbulence and no stratification, one with stratification but no turbulence.

2.   CONCENTRATION OF HEAT

In order to extract useful sork from the sun-heated, upper layer of the ocean, the SSPP must first concentrate this diffuse heat. This concentration takes place within the "boiler". Two calories are skimmed off each gram of warm water "fuel" which enters the boiler, while 280 calories are delivered to each gram of liquid ammonia which enters the boiler, the 280 calories being the heat of vaporization at 20°C and 124 psi. The diffuse heat absorbed by the upper layers of the ocean is thereby concentrated by a factor of 140. Unless special care is taken in the design of this heat concentrator, its capital cost would be prohibitive.

In order to fully appreciate the materials problems encountered in the design of a low-cost heat concentrator, or boiler, we need tc review the physics and engineering involved in heat concentration. First let us look at the physics.

Heat can be induced to flow from the warm sea water into the ammonia only by establishing a downhill temperature gradient from the water into the ammonia. Of the total 20°C temperature

difference between the warm water heat source and the cold water heat sink, only half, namely 10°C, can be spared to induce heat flow; the rest must be available for the heat engine. But of the 10°C for heat flow, one-half can be in the boiler; the other half must be reserved for the condenser. Unfortunately, water is a poor conductor of heat, namely 0.0060 watt/cm°C. With such a low thermal conductivity, a 5°C drop across one cm of water would induce a heat flux of only 0.027 kilowatts of heat per ft^2. At an overall contemplated thermal efficiency of only 2%, we would therefore obtain only 0.0005 kilowatts of power per ft^2; i.e., 2,000 ft^2 of boiler surface would be required per kilowatt output. This is fully 2 orders of magnitude too high. The solution to this dilemma is to bring the warm ocean water close to the heat exchange surface by convection. This is done, of course, by establishing turbulent flow within the heat exchanger tubes. Now turbulent flux cannot extend clear to the surface of the heat exchanger surface. As indicated in Figure 3, at the wall not only is the turbulent flux zero, not only is the derivative of the turbulent flux zero, but also the second derivative of the turbulent flux is zero. One may therefore speak of an effective thickness t of a "laminar" boundary layer across which heat must flow by thermal conduction.

The thickness t of the laminar layer is smaller the higher the flow velocity v through the heat exchanger tubes. But a higher flow velocity means, of course, a higher pumping power

effective wall thickness, t

turbulent flux →

distance from wall
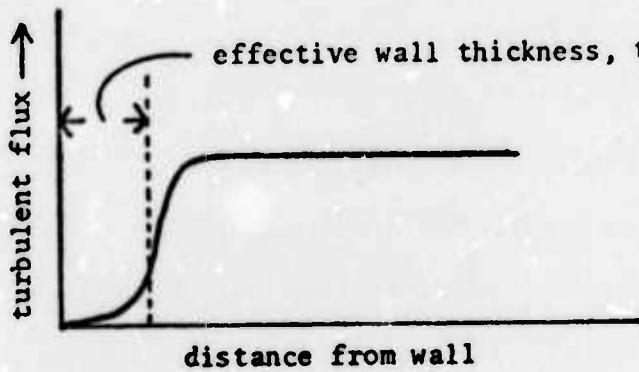
Figure 3

drain upon our gross power output. A consideration of this power
drain brings us to the engineering aspects of the problem of
energy concentration.

The most fruitful way of approaching engineering design
is identical to the approach used by theoretical physicists in
tackling complex problems. One formulates the problem in the
simplest possible way, taking into account all the important fac-
tors but leaving out all irrelevancies. Following this approach,
a little practice enables one to deduce many important features
of an engineering system from merely the structure of the governing
equations, without any detailed calculations. We shall use this
approach to discuss the design problem of heat collection in a
SSPP. We denote by ΔT the total available temperature drop, by
δT_{HX} the temperature drop to be used to drive the required heat
flux Q across the boiler heat exchanger, and an identical temper-
ature drop to drive essentially the same amount of heat across the

-206-

condenser heat exchanger. We denote by U the water velocity in the heat exchanger tubes. Our design objective is to so choose δT_{HE}, δT_E, U, Q to minimize the boiler (and condenser) heat exchanger area A for a specified net power output P. Our governing equations are:

Minimize: $\overset{①}{A}$

Subject to: $\frac{1}{2} f' \, \rho \, C \, U \, \delta T_{HX} \, \overset{②}{A} \geq Q$ (heat flux constraint)

$(\delta T_E/T) \, Q \geq \overset{③}{P} + \overset{④}{f \, \rho \, U^3 \, A}$ (net power constraint)

$2\delta T_{HX}^{⑤} + \delta T_E^{⑥} \geq \Delta T$ (temperature drop constraint)

The structure of these governing equations is completely specified by the following exponent matrix. In this matrix successive columns refer to the unknowns A, U, δT_{HX}, δT_E, Q. Successive rows refer to successive terms, the inequalities all being expressed in a form where unity appears on the "greater than or equal" side.

	A	U	δT_{HX}	δT_E	Q	δ
①	1					1
②	-1	-1	-1		1	3/2
③				-1	-1	1
④	1	3		-1	-1	1/2
⑤			1			3/2
⑥				1		3/2

-207-

This matrix completely determines the δ vector, written to the right of the exponent matrix, defined by the following two properties:

  i.   orthogonal to all columns of exponent matrix;

 ii.   sum of components belonging to objective function
       is unity.

The δ vector is the key to the complete solution to our problem. (C. Zener, Engineering Design by Geometric Programming, Wiley, 1971.)

The above discourse on an approach to engineering design allows us to fruitfully return to the problem of pumping power. The ratio of the fourth to the third component of the delta vector, namely 1/2, gives precisely the ratio, at optimum design, of the pumping power to the net power output. Thus, one-third of the gross power output goes into pumping water in the heat exchanger tubes. This conclusion regarding the fraction of gross developed power used in pumping is completely independent of the numerical values of the various constant, such as the friction coefficient f, the heat transfer coefficient f', etc. Further, from the fact that δ_2 is 3/2, and δ_4 is 1/2, we conclude that at optimized design,

$$A \sim f^{1/2}/f'^{3/2} \quad .$$

If we can roughen the surface so that the heat transfer coefficient f' increases as rapidly as the friction coefficient, f, i.e., so that the ratio f'/f remains constant, such roughening will decrease the area at optimized design according to

-208-

$$A \sim 1/f \quad .$$

As far as this author is aware, no experiments have been performed to determine how to roughen surfaces so as to minimize the ratio $f^{1/2}/f'^{3/2}$. An examination of the physics determining the effective thickness to of the laminar layer suggests that the optimum roughness will have dimensions comparable to t, e.g., ~ 0.01 cm. With commercial smooth surfaces $f = 0.008$, $f' = 0.003$. These values, together with $\Delta T = 20°C$, leads to

$$A = 20 \ ft^2/kw \ net \ output$$

at optimized design. This area corresponds to a heat flux of 10,000 BTU/hr ft^2. We anticipate this can be halved by appropriate surface roughening, to 10 ft^2/kw. This area may fairly be compared to the 100 ft/kw for an artificial solar collector surface described in the opening paragraph.

In the above discussion, we have assumed the surface to be free of scale and of biological fouling. ALCOA has reported their Alclad used in desalination plants has remained free of scaling, and anticipate no scaling problems in SSPP's. We believe biological fouling can be controlled by small additions of Cl_2, or, more appropriately, by electrolytic generation of hypochloric acid within the heat exchanger tubes. Such ideas obviously need verification.

In the above discussion, we have assumed a negligible heat drop is needed to promote ammonia boiling in the boiler, ammonia condensation in the condenser. Such as assumption appears justified

by two recent developments on surfaces. (1) Union Carbide has learned how to mechanically prepare surfaces having permanent sites for the continuous nucleation of bubbles. Such surfaces give nucleate pool boiling with a heat flus of 20,000 BTU/hr ft^2 at a ΔT of only 1°C. (2) Condensing surfaces have recently been designed at this university (by C. Zener and A. Lavi) which require less than a 1°C subcooling to induce condensation rates of 20,000 BTU/hr ft^2. Such surfaces have not yet been tested experimentally.

3.   COLD WATER INTAKE PIPE

Another unique feature of SSPP's is the necessity of bringing tremendous quantities of cold water from the ocean depths in order to dissipate the heat given off by the condensers. We consider here the problems of resistance to the mechanical forces imposed by the ocean environment.

Failure of structures caused by mechanical forces takes place by two distinct mechanisms: (1) failure by plastic yielding, (2) failure by elastic instability, i.e., by buckling. Design for adequate strength to resist plastic yielding is relatively simple. One has merely to insure that the stress everywhere is within safe limits. Design to avoid elastic instability is more subtle. The designer must be sensitized to the various types of instability to which his structure is susceptible. Below we consider several possible instabilities, each of which demands a minimum value of the wall rigidity D, defined by

$$D = \int_{-t/2}^{t/2} E(x) \ x^2 \ dx \quad ,$$

where E is the appropriate elastic constant, essentially Young's modulus, and t is the wall thickness.

Intake Instability
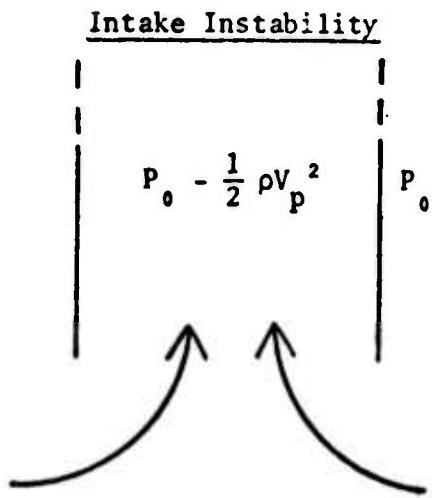
Figure 4

If water is sucked into the cold water pipe by pumps located some distance from the bottom, the interior of the pipe will be at a pressure lower than the external environment. This pressure deficit will be just $\frac{1}{2} \rho V^2$. Viewed as a problem in elastic stability, the pipe is being subjected to an external pressure of $\frac{1}{2} \rho V_p^2$. Any cylinder subjected to a sufficiently large external pressure will fail in the manner depicted in Figure 5.
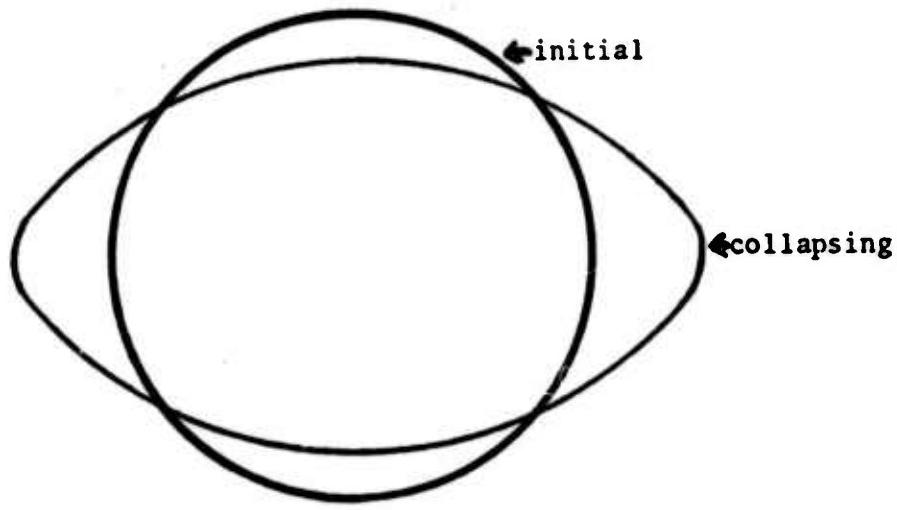
Figure 5

The critical pressure for failure of a perfectly round cylinder
is (Timoshenko and Gere, Theory of Elastic Stability, McGraw-Hill,
1961, 2nd ed., p. 298)

$$\Delta P = \frac{1}{4} \frac{D}{R^3} \quad ,$$

where R is the cylinder radius.   Therefore

$$D \geq 2\rho \, V_p^{\,2} \, R^3 \qquad\qquad\qquad I$$

Collapse by Ocean Current
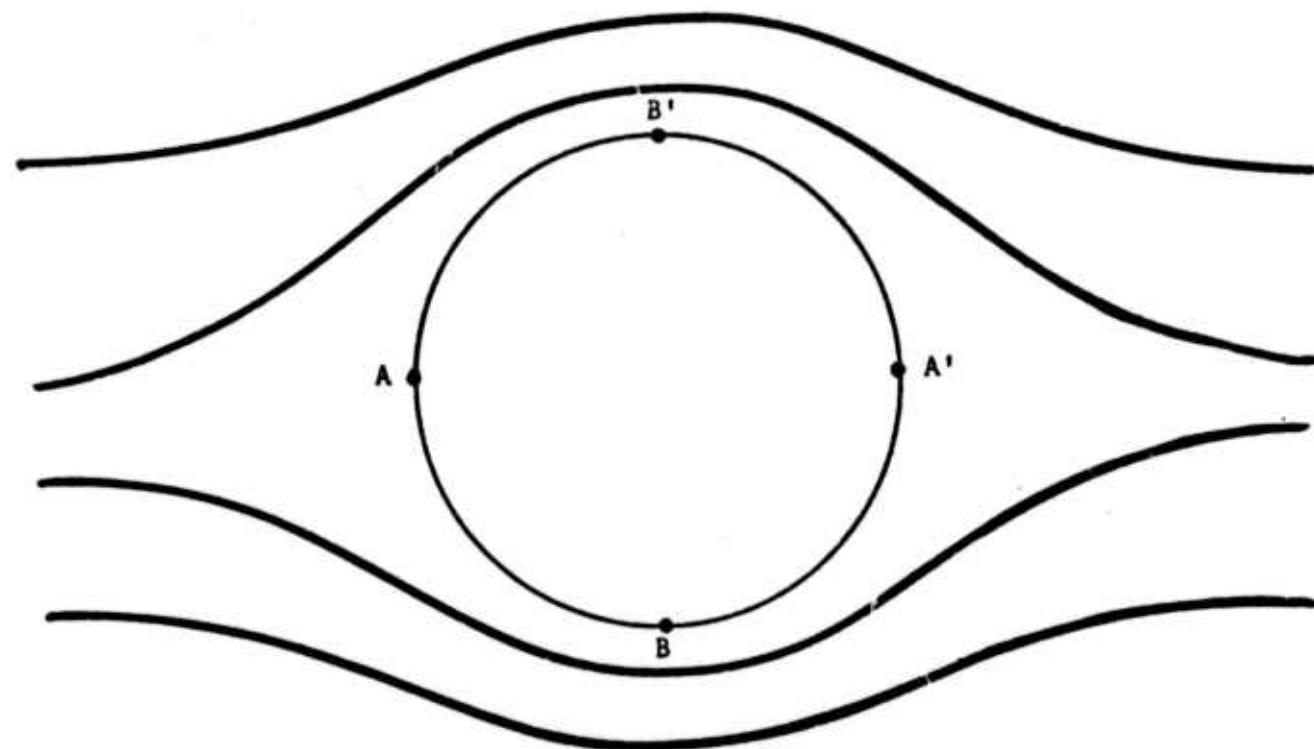
Figure 6

In Figure 6, we represent the streamlined motion of the ocean current past the cold water pipe. The velocity A and A' is zero, is V_B at B and B'. The ocean pressure at A, A' is therefore greater than at B, B' by the amount

$$\Delta P = \frac{1}{2} \rho V_B^2 = \frac{1}{2} \rho (2R/R_A)^2 V_{ocean}^2$$

Whereas the motion around the pipe is not streamlined, the above pressure differential will be approximated. The decrease in the radius at A, ΔR_A, is given by (Timoshenko and Gere, Ibid., p. 281)

$$\frac{\Delta R_A}{R} = \Delta P \cdot R^3/D$$

and hence

$$\frac{\Delta R_A}{R} \left(1 - \frac{\Delta R_A}{R}\right)^2 \simeq 2\rho V_{ocean}^2 \ R^3/D \qquad .$$

The left member of this equation has a maximum value of 4/27, and hence

$$D \geq 14 \ \rho \ V_{ocean}^2 \cdot R^3 \qquad\qquad\qquad II$$

Buckling under Compression
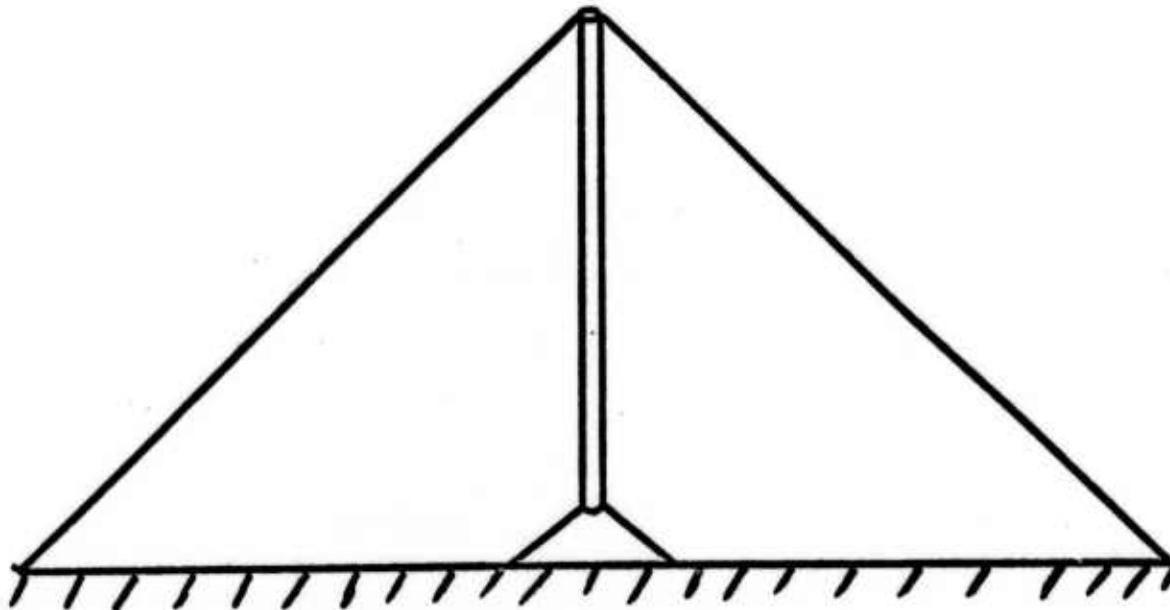
Figure 7

The top and bottom of the cold water must certainly be anchored, as indicated in Figure 7. In order to estimate the ocean current induced stresses in such an anchored pipe, we shall assume the current to have a constant velocity V_0 at all depths. Such a current will produce a bending moment across the mid-plane of the pipe of $\sim\frac{1}{4} L^2 R \rho V_c^2$. The compressive force per unit circumference on the up-current side of the pipe is hence $\sim(1/8\pi)(L^2/R)\rho V_0^2$. But if local buckling is to be avoided, this compressive force cannot exceed $(2.4/tR)D$. (Timoshenko and Gere, Ibid., pp. 468-484). We therefore conclude that in order to avoid local buckling

$$D > \pi^{-1} \rho V_{ocean}^2 (L/4)^2 t \qquad\qquad \text{III}$$

Review of Elastic Instabilities

All three criteria for elastic stability, I, II, and III, require a high value for wall rigidity D, comparable to that given by a 1" wall thickness of a steel pipe. Such a wall is, however, ten times thicker than is required merely to resist plastic deformation. We are thereby led to the concept of a duplex structure. A possible duplex structure would be, for example, two concentric thin pipes with an appropriate filler, as illustrated in Figure 8.
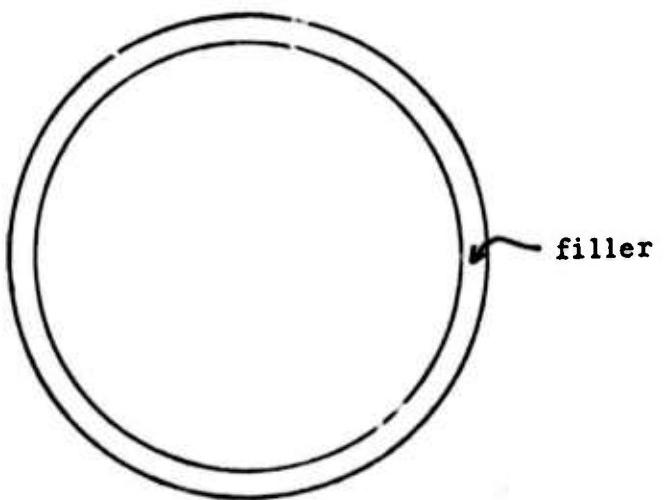
Figure 8

Considerable work is required to develop such a duplex wall that will minimize cost and satisfy the rigidity conditions I, II, and III.

Acknowledgement

ON INCREASING THE HEAT TRANSFER AT THE SEAWATER
SIDE OF THE BOILER IN THE SEA THERMAL GRADIENT SYSTEM

J. P. Hirth

Zener pointed out the tremendous advances in improving the heat transfer coefficient at the condenser side of the system and in the working fluid side of the boiler. The principal remaining impedance appears to be on the seawater side of the boiler. He further mentioned optimization techniques including surface roughening to improve heat transfer at the last mentioned site.

Two other possibilities are suggested which might merit study. One would be to place small ridges on the metal to produce either turbulence or cavitation at sites such as A, either of which would increase the heat transfer.
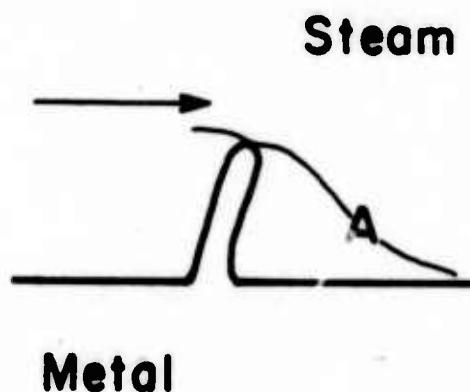
Figure 1

A second possibility, with perhaps more dramatic conse-
quences, would be to discharge hydrogen cathodically on the sea-
water side of the metal. Analogous to the increase of heat trans-
fer at the boiling interface at the onset of bubble nucleation,
this could provide an order of magnitude or more increase in heat
transfer rate. Since this site represents the high impedance
point in the process, overall rates could be similarly increased
and working areas similarly decreased. The process would require
energy for the electrochemical process, part of which would be
recovered by using the hydrogen as fuel. Also, an anode (porous
platinum for example) would be required. However, the process
would appear to merit an optimization test

As noted by Zener in a discussion of this idea, chlorine
could perhaps be discharged at the anode to aid in controlling
the concentration of organic matter in the system to avoid fouling.

Acknowledgement

MATERIALS PROBLEMS IN EXTRACTING POWER
FROM OCEAN THERMAL GRADIENTS

R. Bleiden and C. Zener

1.0   What are the overall chances of success?

The probability is very high that electric power can be
generated at a lower cost than by fossil fueled or nuclear plants.
Such success would lead to energy-intensive industries being
developed in those Caribbean countries friendly to the U.S.
Such development would relieve the power demand within the U.S.
The materials problems which must be solved for this success are
outlined in 2.1.

2.0   What are the primary materials problems?

2.1   We must develop low cost fabrication methods for preparing
surfaces with high heat transfer boiling and condensing coeffic-
ients. Such surfaces have been prepared in limited quantity with
boiling and condensing coefficients as high as 10,000 BTU/hr ft °F.

2.2   We must develop practical methods of preventing biological
fouling of the sea-water side of the above heat exchange surfaces.

2.3   We must develop materials and fabrication techniques for
the cold water intake pipes. This pipe must be 40'-80' diameter,
$\sim$3,000' long, and have sufficient resistance to buckling to with-
stand the forces arising from the ocean currents.

2.4   The transmission of electric power to the continental U.S.A. might only be economically feasible if superconducting underwater transmission cables are developed. Materials for such a cable are the current bottleneck.

2.5   We must learn how to appropriately roughen the sea-water side of the boiler and condenser heat exchange surfaces so as to raise the heat exchange coefficient with respect to the friction coefficient. We have ideas about how this is to be achieved, but no experiments have been conducted to date.

2.6   Development of turbine materials that will resist corrosion by the working medium in the heat engine.

2.7   Development of a low cost electrolysis cell for the decomposition of water into hydrogen and oxygen gas in the event this becomes the most economic way of transporting energy from SSPP's to the U.S.A.

2.8   Development of methods of transporting hydrogen by pipelines without danger of hydrogen-embrittlement.

Acknowledgement

ENERGY STORAGE VIA FLYWHEELS

J. J. Gilman

Abstract

A method for energy storage that has considerable versatility is the flywheel. The elements of flywheel energy storage are discussed and the pros and cons are discussed in terms of specific idealized configurations. An expression for the maximum power output is derived which shows that flywheels are capable of delivering approximately 10^6 times as much power as very good batteries. Because of this and other features, flywheels complement the performances of batteries. This makes hybrid battery-flywheel systems attractive for energy storage.

ENERGY STORAGE VIA FLYWHEELS

J. J. Gilman

I.   Introduction

The versatility of batteries as energy storage devices has been and remains very attractive. However, they have certain limitations which provide opportunities for other devices. One of these which has considerable versatility is the flywheel. Moreover, many of the strengths of flywheels complement the weaknesses of batteries. This makes battery-flywheel hybrids attractive. For example, although good batteries store energy well, they store power poorly because they have appreciable internal resistances, and because they cannot be discharged rapidly without degrading their internal structures.

The purpose of this discussion is to describe some of the properties of flywheels, to estimate their present and future efficiencies, and to compare their characteristics with those of batteries.

II.   Elements of Flywheel Storage

The best known form of a flywheel is a rotating solid disk. However, this device has at least two disadvantages for many circumstances. First, the strongest available materials at present are fibrous and hence highly anisotropic. Second, homo-

geneous rotating disks are dangerous to use because their failures generate massive high velocity projectiles. Therefore, it is desirable to consider a variety of flywheel forms.

Six representative or limiting forms will be considered:

a) rod (rotation axis parallel to thickness)

b) hoop (rotation axis normal to plane)

c) solid disk (rotational axis normal to plane)

d) tape disk (rectangular tape wrapped to make disk)

e) splayed disk (disk shaped brush)

f) disk with contour shaped to give constant stress throughout

For each of these, the energy that can be stored per unit weight and per unti volume will be derived, plus the partition of stored energy between rotational kinetic energy and strain potential energy. Sketches of the five forms are given in Figure 1.

a.   ROD

A slender rod as shown in Figure 1 has kinetic energy:

$$T_1 = \int_0^R A\rho\omega^2 r^2 dr = \frac{A\rho\omega^2 R^3}{3}$$

where: A = cross-section area

ρ = mass density

ω = angular rotation in radians per second

R = half-length

this leads to a tensile stress at any radial position, r of:

$$\sigma(r) = \rho\omega^2 \int_r^R r\,dr = \frac{1}{2}\rho\omega^2(R^2 - r^2)$$

and a maximum stress at the center, $r = 0$:

$$\sigma_{m_1} = \frac{1}{2}\rho\omega^2 R^2$$

The stress in turn leads to stored strain energy (where E is the Young's modulus):

$$V_1 = \int_{-R}^{+R}\left(\frac{\sigma^2}{2E}\right)A\,dr = \frac{A\rho^2\omega^4}{8E}\int_0^R (R^2 - r^2)^2\,dr = \frac{2}{15}\left(\frac{A\rho^2\omega^4 R^5}{E}\right)$$

The ratio of this strain energy to the kinetic energy is:

$$\frac{V_1}{T_1} = \frac{2}{5}\left(\frac{\sigma_m}{\rho}\right)$$

so the strain energy is small compared with the kinetic energy. Even if the σ_m reaches the intrinsic cohesive strength $E/10$, the strain energy is only 4% of the kinetic energy. This is because large strains are present only near the rotation axis.

The specific kinetic energy stored per unit weight (which is very nearly equal the specific stored energy is:

$$T_1 = \frac{1}{3}\left(\frac{\sigma_m}{\rho}\right)$$

so it may be seen that flywheel storage efficiency depends only on specific strength.

b.　　HOOP

In this case the mass is placed as far away from the center of rotation as possible (Figure 1b) and the kinetic energy becomes:

$$T_2 = \pi \rho A \omega^2 R^3$$

while the maximum stress is (assumed to be uniform for a thin hoop):

$$\sigma_{m2} = \rho \omega^2 R^2$$

and the strain energy is:

$$V_2 = \frac{\pi A \rho^2 \omega^4 R^5}{E}$$

so the strain/kinetic energy ratio becomes:

$$\frac{V_2}{T_2} = \frac{1}{2} \left(\frac{\sigma_m}{E} \right)$$

which is larger than for the rod because the strain is now uniformly distributed in the rotating material. However, even in the extreme case of $\sigma_m = E/10$, the strain energy is only 5% of the kinetic energy.

The specific kinetic energy in this case is:

$$T_2 = \frac{1}{2} \left(\frac{\sigma_m}{\rho} \right)$$

and hence not as high as for the case of the rod.

However, for the same volume of material (or weight at constant ρ) the hoop radius, R_2 relative to the spin radius of

rod, R_1 is:

$$R_2 = R_1/\pi$$

therefore, the kinetic energy ratio at constant device size is:

$$\left(\frac{T_2}{T_1}\right)_{R,\omega} = 3\pi$$

so, for a given device size and speed, a hoop is nearly 10 times more efficient than a rod.

If stress and size are held constant rather than speed and size, then:

$$\left(\frac{T_2}{T_1}\right)_{R,\sigma} = \frac{3\pi}{4}$$

so a hoop is about 2.5 times more efficient than a rod on this basis.

c.   THIN DISK

For a thin disk of thickness, t (Figure 1c) the kinetic energy is:

$$T_3 = \frac{\pi\rho\tau\omega^2 R^4}{4}$$

and the radial and tangential components of the stress field (the z-component is neglected since the disk is thin):

$$\sigma_r = (\frac{3+\nu}{8})\ \rho\omega^2\ (R^2 - r^2)$$

$$\sigma_\theta = (\frac{3+\nu}{8})\ \rho\omega^2 R^2 - (\frac{1+3\nu}{8})\ \rho\omega^2 r^2$$

where ν = Poisson's ratio, so the maximum stresses at the center are:

$$\sigma_m = \sigma_\theta(r=0) = \sigma_r(r=0) = (\frac{3+\nu}{8})\,\rho\omega^2 R^2$$

In this case the strain energy depends on Poisson's ratio and is given by:

$$V_3 = \frac{\pi t}{E} \int_0^R (\sigma_r^2 + \sigma_\theta^2)\,r\,dr$$

Letting:

$$A = (\frac{3+\nu}{8})\rho\omega^2$$

$$B = (\frac{1+3\nu}{8})\rho\omega^2$$

this becomes:

$$V_3 = \frac{\pi t R^6}{6E}\,(4A^2 - 3AB + B^2)$$

$$= \frac{.075\pi\rho^2\omega^4 R^6}{E} \qquad\qquad (\nu = 1/3)$$

the term in parentheses equals 0.46, 0.45, and 0.44 for $\nu = 1/4$, 1/3 and 1/2, respectively, so the middle value is quite representative and the potential energy is:

$$V_3 \simeq \frac{0.075\pi\rho^2\omega^4 R^6 t}{E} \qquad\qquad (\nu = 1/3)$$

so the strain/kinetic energy ratio is:

$$\frac{V_3}{T_3} = 0.71\,(\frac{\sigma_m}{E})$$

which is higher than for either the **rod** or the hoop.

The specific kinetic energy is:

$$T_3 = 0.6 \ (\frac{\sigma_m}{\rho})$$

making the solid disk is more efficient than either the rod or the hoop.

The storage efficiency on a size basis (constant speed) is:

$$\left(\frac{T_3}{T_2}\right)_{R,\omega} = \frac{1}{4}(\frac{R}{t})$$

which can be large for a thin disk.

The size efficiency at constant maximum stress is:

$$\left(\frac{T_3}{T_2}\right)_{R,\sigma} = 0.6(\frac{R}{t})$$

which again is large for a thin disk.

d.   **TAPE DISK**

A convenient way to make a flywheel from a fibrous material is to wind pre-fabricated tape around a shaft in the form of a disk (Figure 1d). Such a disk is the same as a thin disk that has no ability to support radial stresses; or the same as a set of concentric non-interacting hoops. The values of the pertinent quantities are as follows:

$$T_4 = \frac{\pi}{4} \ \rho t\omega^2 R^4$$

$$\sigma_m = \rho\omega^2 R^2$$

-228-

$$V_4 = \frac{\pi \rho^2 t \omega^4 R^6}{3E}$$

$$\frac{V_4}{T_4} = 0.33 \left(\frac{\sigma_m}{E}\right)$$

$$T_4 = \frac{1}{4}\left(\frac{\sigma_m}{\rho}\right)$$

$$\left(\frac{T_4}{T_2}\right)_{R,\omega} = \frac{1}{4}\left(\frac{R}{t}\right)$$

$$\left(\frac{T_4}{T_2}\right)_{R,\sigma} = \frac{1}{4}\left(\frac{R}{t}\right)$$

2.   SPLAYED DISK (Brush)

This is similar to a thin disk that cannot support radial stresses. Thus it is an idealized set of thin rods or a brush. The values of the pertinent quantities for this case are:

$$T_5 = \frac{\pi}{4} \rho t \omega^2 R^4$$

$$\sigma_m = \left(\frac{3+\nu}{8}\right) \rho \omega^2 R^2 = 0.42 \rho \omega^2 R^2 \qquad (\nu = 1/3)$$

$$V_5 = \frac{\pi t}{E} \int_0^R \sigma_\theta^2 \, rdr = \frac{\pi}{6E}\left(\frac{3+\nu}{8}\right)^2 \rho^2 \omega^4 R^6 t = \frac{0.09 \rho^2 \omega^4 R^6 t}{E}$$

$$\frac{V_5}{T_5} = 0.27 \left(\frac{\sigma_m}{E}\right)$$

$$T_5 = 0.6 \left(\frac{\sigma_m}{\rho}\right)$$

$$\left(\frac{T_5}{T_2}\right)_{R,\omega} = \frac{1}{4}\left(\frac{R}{t}\right)$$

$$\left(\frac{T_5}{T_2}\right)_{R,\sigma} = 1.2\left(\frac{R}{t}\right)$$

-229-

f.   DISK SHAPED FOR CONSTANT STRESS

Jakubowski (1972) has shown that a rotating disk with a flat bell-shaped profile has the same stress at all points and therefore optimizes both the energy stored per unit volume and per unit weight. If the thickness of such a disk is t_0 at the axis of rotation, then its profile is given by:

$$t = t_0 \, e^{-r^2/2c} \qquad\qquad (c = \sigma_m/\rho\omega^2)$$

its performance depends on its size, but in the limit of large R its specific kinetic energy is:

$$T_6 = \sigma_m/\rho$$

thus it represents the ideal flywheel since this is the maximum possible storage density.

g.   COMPARISON OF CHARACTERISTICS

The storage efficiencies of various forms of flywheels are listed in Table 1. The energy stored per unit weight ranges from 0.25 to 1.00 times the specific strength. For all real materials with $\sigma_m < E/10$ the amount of potential energy is small compared with the kinetic energy. The energy stored per unit volume swept out by the rotating body ranges from a negligible amount to σ_m.

The disk with a shaped contour is clearly the ideal form, but it requires an isotropic material for its construction. The strongest available materials are fibers for which the form that

-230-

is the best compromise between ease of construction and storage efficiency per unit weight is the rotating hoop. A better choice if volume is critical is the tape disk.

III.   FLYWHEEL PERFORMANCE

For specific energy storage a disk flywheel with a strength of $1.5 \times 10^6 \#/in^2$ and specific gravity = 3 can store 350 watt-hours/# which is about 100 times as much as a practical lead-acid battery. This assumes an isotropic material and does not allow for associated bearings and containers. The use of a fibrous material in the form of a hoop and allowing equal weight for associated equipment reduces this to about 90 watt-hrs/# which is comparable with the most advanced present batteries and a factor of 10-20 better than lead-acid batteries.

The absolute upper limit for feasible flywheel storage would be given by a fibrous material with a strength of $5 \times 10^6 \#/in^2$ and specific gravity = 2. This would yield (for a hoop): 900 watt-hrs/# ideally or about 450 watt-hours/# in a machine.

It is concluded that flywheels can definitely compete with batteries in terms of storage efficiency as pointed out by numerous previous authors. Next, consider the power output that a flywheel can yield.

Since a flywheel will be built of very strong materials and will be a compact rigid structure, the limitation on power output will probably be determined by the properties of the load machinery that is attached to it. However, an approximate

-231-

upper limit will be imposed by the maximum torque that the shaft which supports the flywheel can withstand.

For a shaft of radius R_o and shear strength σ_s, the maximum torque that can be withstood is:

$$\tau_{shaft} = \frac{2\pi}{3} \sigma_s R_o^3$$

and if p is the angular momentum of the flywheel:

$$p = 2\pi\rho\omega t \int_0^R r^2 dr$$

The torque caused by a change in speed of the flywheel is:

$$\tau_{flywheel} = 2\pi\rho\dot{\omega}t \int_0^R r^3 dr = \frac{\pi}{2} \rho\dot{\omega}tR^4$$

Equating these torques gives an expression for the maximum permissible rate of change of the speed:

$$\dot{\omega}_{max} = \frac{4}{3} \left(\frac{\sigma_S}{\rho R t}\right) \left(\frac{R_o}{R}\right)^3$$

The power output is the rate of change of the kinetic energy so if the shaft strength equals the flywheel strength $(\sigma_s = \sigma_m/2)$:

$$P_{max} = \frac{dT}{dt} = \frac{\pi}{2} \rho\omega tR^4\dot{\omega}_m = \frac{\pi}{3} R_o^3\sigma_m$$

where the maximum value of ω is determined by the maximum tolerable stress in the flywheel:

$$\omega_{max} \simeq \frac{1}{R}\left(\frac{2\sigma_m}{\rho}\right)^{\frac{1}{2}}$$

To estimate a numerical value for P_{max}, let $t = R_O = R/10$, and consider a flywheel that weighs 10#. Then $R = 17$ cm, using the properties of the first paragraph of this section:

$$\omega_m \simeq 1.6 \times 10^6 \text{ rad/sec}$$

$$P_m \simeq 5 \times 10^8 \text{ watts}$$

This may be compared with present high performance batteries whose maximum delivery rates are about 30 watts/# or in this case 300 watts. Thus a high storage density flywheel can deliver about 10^6 more power than a high storage density battery.

Since R_O and R scale together, the maximum power output scales with the square of the flywheel radius, the 3/2 power of the strength, and inversely with the square root of the density. Thus large flywheels can deliver very large amounts of power. Batteries cannot compete in this respect and condenser banks trail far behind.

IV.   SOME PROS AND CONS

Advantages of flywheels as storage devices are:

a. high ideal storage density - approximately 1000 watt
   hours/#

b. very high peak-power output; especially as compared
   with batteries; and more especially compared with
   fuel cells

c. temperature independent operation

-233-

d. unlimited shelf life when uncharged

e. rapid charging rates

f. unlimited operating life; except for bearing wear and strength fatique

g. no environmental pollution

h. relatively inexpensive raw materials

i. flexible input-output modes

    1. mechanical

    2. hydraulic

    3. AC-DC electrical

j. cost per unit capacity decreases with increasing size

k. fail-safe design is feasible; chemical explosions, gas explosions, fire hazards, and fires not a problem.

Disadvantages are:

a. high cost per unit storage capacity in small sizes

b. limited charged shelf-life - approximately one week for moderate sizes

c. evacuated containers are needed for low average power output applications - for moderate to large devices these can be self-pumped.

Acknowledgement

-234-

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Chemical Society, p. 1141 (1972).

TABLE 1 - FLYWHEEL STORAGE EFFICIENCIES

FORM	MAXIMUM SPECIFIC KINETIC ENERGY	STRAIN/KINETIC ENERGY RATIO	MAXIMUM KINETIC ENERGY PER VOLUME SWEPT OUT
ROD	$0.33\,(\sigma_m/\rho)$	$0.40\,(\sigma_m/E)$	$0.21\,\sigma_m\,(t/R)$
HOOP	$0.50\,(\sigma_m/\rho)$	$0.50\,(\sigma_m/E)$	$1.00\,\sigma_m\,(t/R)$
DISK – SOLID	$0.60\,(\sigma_m/\rho)$	$0.71\,(\sigma_m/E)$	$0.59\,\sigma_m$
DISK – TAPE	$0.25\,(\sigma_m/\rho)$	$0.33\,(\sigma_m/E)$	$0.25\,\sigma_m$
DISK – SPLAYED	$0.60\,(\sigma_m/\rho)$	$0.27\,(\sigma_m/E)$	$0.59\,\sigma_m$
DISK – SHAPED FOR CONST. STRESS	$1.00\,(\sigma_m/\rho)$	$0.50\,(\sigma_m/E)$	$1.00\,\sigma_m$
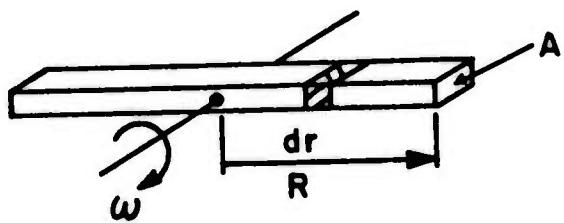
(A) ROD
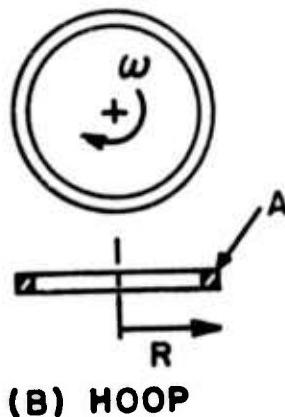
(B) HOOP
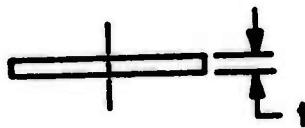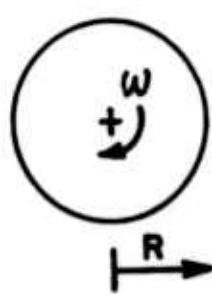
(C) SOLID DISK
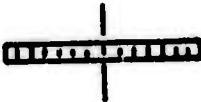
(D) TAPE DISK
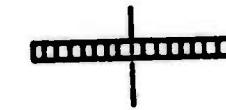
(E) SPLAYED DISK

FIGURE I — FORMS OF FLYWHEELS

CHEMICAL SYSTEMS FOR STORAGE
OF SOLAR ENERGY

J. L. Margrave

Abstract

Thermodynamic data are being reviewed for some simple
systems of energy storage, including the possibility of using
a water-sulfuric acid working fluid from which water is removed
by daytime evaporation to produce concentrated sulfuric acid
and then, heat is recovered by dilution of the concentrated
H_2SO_4, a process which is exothermic by 15-23 KPM, depending on
dilution. Other suitable chemical reactions or phase transfor-
mations will be considered.

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MATERIALS PROBLEMS RELATING TO
HIGH TEMPERATURE OXIDE ION CONDUCTING FUEL CELLS
FOR THE ELECTROCHEMICAL COMBUSTION OF HYDROGEN

R. A. Huggins and R. L. Coble

Abstract

The current status of the development of high tempera-
ture fuel cells utilizing solid electrolytes for the electro-
chemical combustion of gaseous fuels is reviewed. Special
attention is given to the materials problems relating to cells
employing doped ZrO_2 as the electrolyte. Also included are
comments relating to cost estimates for such systems. It is
concluded that oxide ion-conducting solid electrolyte fuel
cells might be particularly attractive for the combustion of
hydrogen, but that there are still serious problems relating
to the development of adequate materials to use as inter-
connectors and for the electrode on the oxidizing side. In
addition, costs will be critically dependent upon the develop-
ment of inexpensive ceramic fabrication methods.

MATERIALS PROBLEMS RELATING TO
HIGH TEMPERATURE OXIDE ION CONDUCTING FUEL CELLS
FOR THE ELECTROCHEMICAL COMBUSTION OF HYDROGEN

R. A. Huggins and R. L. Coble

I. Introduction

An appreciable amount of attention is currently being given to increased utilization, conversion and storage of solar energy. Several of the schemes that have been proposed for making better utilization of the available intermittent solar energy arriving upon the earth involves the storage of energy in chemical form by the electrolysis of water to produce hydrogen and oxygen. These species can be stored and recombined to produce either heat or electricity locally, or either one or both could be transmitted appreciable distances and utilized for that purpose at some remote location. In general some storage system is needed because the power demand schedule does not conform to the intermittent delivery rate.

One of the methods whereby this chemical energy can be converted into electrical power involves the use of an electrochemical fuel cell. Under favorable conditions, fuel cells can have considerably larger values of intrinsic efficiency than is the case with other types of conversion systems which can not exceed the Carnot efficiency.

Various types of hydrogen fuel cells have been proposed. They fall into two major categories; those involving the utilization of liquid electrolytes, which operate at low to intermediate temperatures, and a second group utilizing a solid electrolyte and operating at higher temperatures. In general, a critical consideration in liquid electrolyte fuel cell systems is the need for heterogeneous catalysts at one or both of the electrodes because of relatively slow electrode kinetics. Platinum is typically used for this purpose, and its price and availability provide a large incentive for the discovery and development of substitute materials.

High temperature solid electrolyte fuel cells, on the other hand, do not have this problem, as electrode processes proceed much more rapidly at elevated temperatures. Such fuel cells also have additional advantages. Since there are no liquid phases present, corrosion and sealing problems are greatly reduced. Likewise, the composition of the electrolyte does not depend upon the constitution of the fuel, and there are no problems involving three phase (gas-liquid-solid) interfaces.

On the other hand, solid electrolyte fuel cells do have the disadvantage of requiring operation at high temperatures (typically 800-1000°C) due to the high resistance of the solid electrolyte at lower temperatures. The most prominent example of high temperature solid electrolytes is doped zirconium dioxide (ZrO_2), which, in the cubic modification, is an excellent con-

ductor of oxide ions.

This material and its unusual properties have been known for many years. Nernst and his coworkers discovered the high conductivity of ZrO_2 containing 15% Y_2O_3 before the beginning of the present century, and utilized this conducting oxide in the light source called the "Nernst glower". By 1914, Ruff and co-workers discovered that both the mechanical and electrical con-ductivity of ZrO_2 could be improved by appropriate addition of Y_2O_3, CaO or MgO. The earliest report of the utilization of these materials for fuel cell purposes was in a paper by Baur and Preis (1937).

A wave of interest in ZrO_2-based solid electrolyte fuel cells began in the early 1960's with the paper by Weissbart and Ruka (1962). Other early work can be found in the papers by Binder et al. (1963), Archer et al. (1965), Schachner and Tannenberger (1965), Rohland and Möbius (1968), Eysel and Kleinschmager (1969), and Böhme and Rohr (1969). More recent developments have been summarized in the papers by Huff (1972), Tannenberger (1972), Sverdrup et al. (1972) and Markin (1972).

II.   Present Approaches to Solid Electrolyte Fuel Cells

   A.   General Principles Relating to Solid Electrolyte Fuel Cells

Fuel cells transform chemical energy into electrical energy by an arrangement in which at least one of the ionic constituents involved in a chemical reaction is transported through an electrolyte phase within the fuel cell system.

-244-

Corresponding electronic current is caused to flow through an external electrical load and thus becomes accessible to do work. The electronic conductivity of the electrolyte must be small to give small internal electrical losses. The general arrangement of such a system is illustrated schematically in Figure 1. In this example, the chemical reaction involved in the oxidation of hydrogen occurs by the transport of oxygen ions from the positive electrode side of the cell which contains a source of oxygen through the solid electrolyte to the negative electrode side. Upon arrival at the negative electrode, these ions give up their electrons and react with hydrogen to form water.

The chemical free energy change involved in this reaction can be expressed as

$$\Delta G = NkT \ln\left(\frac{p_{O_2}^{I}}{p_{O_2}^{II}}\right) \tag{1}$$

where N is Avogadro's number and p_{O_2} is the local value of the oxygen pressure. This free energy change is simply related to the open circuit voltage of the cell E^0 under conditions of no current flow by

$$E^0 = -\frac{\Delta G}{nF} \tag{2}$$

If current passes through the cell (and therefore also through the external electrical load) the actual cell voltage is reduced by the IR loss related to the transport of the ionic species through the electrolyte-electrode system. One can then

write

$$E = - \left(\frac{NkT}{nF}\right) \ln\left(\frac{p_{O_2}^{I}}{p_{O_2}^{II}}\right) + IR \qquad (3)$$

where E is the voltage across the external load.

Since the power in the external load circuit can be written as

$$P = IE \qquad (4)$$

it is obvious that one of the critical features of such a system is the value of the internal resistance, R. The primary source of internal resistance involves the ionic transport through the electrolyte and the generally accepted objective is to reduce the electrolyte resistance to less than about 0.1 ohm-cm^2. A second voltage loss could also arise from electrode polarization at high current flow.

As will be discussed in more detail later, all present developments are based on the use of the cubic phase of zirconium dioxide (ZrO_2) doped with other oxides to increase the ionic con-ductivity. Such cells typically operate at about 1000°C where the resistivities of these solid electrolytes are in the range 2-5 ohm-cm. As a result, it is clear that electrolyte thicknesses less than 200 microns would be desireable.

B. Design Approaches

Because of problems related to sealing and fabrication, the development programs on high temperature solid electrolyte

-246-

fuel cells have chosen to use tubular shapes rather than flat plate configurations. Earlier work involved the fabrication of short lengths of thin electrolyte tubes which were then connected together to produce a series of individual cells. When this approach is used, problems have been encountered relating to mechanical strength and gas permeation. It has generally been found that the minimum practical thickness of free-standing electrolyte layers is about 500 microns. Electrolyte tubes in this range have been produced by standard pressing and sintering methods followed by machining to reduce the wall thickness. Another approach has been the use of plasma spraying techniques to fabricate small tubes in this range.

More recently, development efforts have centered upon the support of thin films of electrode and electrolyte materials upon porous substrates. These substrates can be considerably thicker and provide mechanical strength to support thin layers. Typical substrate materials are slip-case or extruded stabilized zirconia ceramics with about 30% porosity. The electrode, electrolyte and interconnecting layers are deposited upon the substrate in thicknesses on the order of 10-50 microns by any of several methods, including chemical vapor deposition, electrophoretic deposition, reactive sintering or flame or plasma spraying.

Since, in order to optimize the power output of such systems, it is expected that they would be operating at a current

density of 400-800 milliamperes per cm^2, the collection and handling of this amount of current is an important consideration in the design of the cell system.

In order to reduce the current collection problems, present designs of oxide ion-conducting solid electrolyte fuel cells involve the fabrication of a series of small cells upon a larger porous substrate by the deposition of a sequence of thin films. The general arrangement utilized in this approach is illustrated schematically in Figure 2.

These layers are deposited upon the substrate in sequence using appropriate masking or other techniques for producing the desired geometry. This method of fabrication of multi-layer structures involves repeated heating and cooling cycles to temperatures of about 1400°C and the system will probably also be cycled many times during its service life. Thus it is obvious that careful attention must be given to the matter of the compatibility of the thermal expansion coefficients of the various materials involved.

The required properties and special problems relating to the component materials used in these cells are discussed in the next section.

III.   Materials for Fuel Cell Components

A.   The Electrolyte

Although there are numerous ionic conductors available, most fuel cells under development use air (oxygen) as one of the

-248-

reactants. The high temperature fuel cells (operating at about 1000°C) primarily utilize zirconia doped with different elements to form a stable cubic phase with high ionic conductivity for oxygen. The requirement for the electrolyte in a battery or cell is that the resistance should be less than 0.1 ohm-cm^2. The resistivities of doped zirconias give values greater than 10 ohm-cm, therefore, relatively thin films of the electrolyte must be fabricated for use. Calcia stabilized zirconia has been widely investigated and is of greatest interest from an economic point of view because it is of lower cost than other phases. Etsel and Flengas (1970) have reviewed the properties of previously investigated electrolytes; they cite Carter and Roth's (1968) data on the aging characteristics of calcia stabilized zirconia. In addition to having a relatively high resistance the calcia stabilized phase also increases its resistance during operation. With a base line resistivity of the order of 100 ohm-cm the calcia stabilized zirconia should be utilized in films with thicknesses in the range of 10 microns. Other compositions have been surveyed for use as electrolytes but the yttrium, ytterbium and scandium oxides as additions have been found to give the highest conductivities in stable cubic zirconia phases. With resistivities of the order of 10 ohm-cm at 1000°C these compositions could be utilized in cells with film thicknesses of the order of 100 microns.

Of the materials problems which have been identified in fuel cell construction and use, work on electrolytes has been

most extensive, consequently there are fewer technical problems identified in the current state of the art with the electrolyte than with the other fuel cell components. Basic problems associated with high conductivity electrolytes are expense in fabrication and high materials costs.

B. Electrodes

The electrodes are affixed to the opposite sides of the electrolyte as shown in Figure 1; they collect the current from the many square centimeters of area of electrode surface and convey it into a compact current lead and without excessive internal resistance provide for the electronic exchange at the electrolyte surface with the reactant and product gases without inhibiting gas flow. For current collection the resistivity of the electrodes should be less than 10^{-3} ohm-cm. Conductivities in this range can be achieved for many metals in porous form. The electrodes are made porous to permit the gases to easily move from their feed channels to the electrode: electrolyte interfaces. The porosity introduced to make the electrodes permeable reduces the effective conductivity in the plane of the electrode; this limits the length of a cell which can be usefully fabricated. As shown in Figure 2 cells are generally stacked in series sequence in order to increase the voltage rather than the current along the length of a stack of cells. For each side of the electrolyte the electrodes must be chemically compatible with the electrolyte as well as with the reactant atmosphere. A

thermal expansion match is also needed in order to permit thermal cycling of the overall fuel cell.

Electrodes for the fuel side of the cell in which the atmosphere is kept reducing have been made from nickel, cobalt, and cermets involving nickel: zirconia and cobalt: zirconia as well as noble metals and have worked satisfactorily. For reasons of cost, power producing fuel cells would obviously make use of the nickel base electrodes that have shown satisfactory performance in tests conducted to date.

Electrodes for the oxidizing side of the electrolyte have presented far greater problems. A number of noble metal electrodes have been utilized. Tannenberger (1972) has reviewed the performance achieved with platinum, palladium, and silver in particular. All of these are excessively expensive for potential use in a power producing fuel cell. Silver is attractive because it provides high oxygen solubility and diffusivity; this would permit its use in a continuous film form on top of the electrolyte. However, its volatility at the temperatures of interest precludes its use. Tedmon et al. (1969) reported on a cell with a praseodymium cobaltite electrode ($PrCoO_3$) which operated electrically for nine months but spalled on cooling. Lanthanum strontium cobaltite has also been found to be adequate initially; but it undergoes aging, increasing in resistance when in contact with zirconia electrolytes in use.

Of the many electrodes that have been studied there is one promising survivor of the set: tin doped indium oxide.

-251-

Sverdrup et al. (1969) and Maskalick et al (1970) have reported 1000 hour stability of oxidizing electrodes of the indium oxide base; other investigators have also found satisfactory use with indium oxide electrodes.

In summary, the state of the art at this time affords a suitable electrode (nickel) for the reducing atmosphere side of the cell. There appears to be a promising one (doped indium oxide) for the oxidizing side; however, long term testing has not yet been conducted to establish the acceptability of these electrodes. Furthermore, indium is quite expensive and would represent the most significant materials cost in the system described.

C. Interconnectors

The cell configuration illustrated in Figure 2 shows the series stacking to increase the voltage, which alleviates problems due to increasing the current. This is important due to the limited conductivity available in porous thin film electrodes. The interconnectors serve the function of connecting cells plus to minus; they must be made of an electronically conducting material which has an expansion match with the electrolyte and the electrodes, as well as being stable in both the oxidizing and reducing environments to which it is exposed on the opposite sides of the cell. This is a relatively recently identified material requirement; as a consequence relatively little work has been done on such materials. The requirements are only slightly more demanding than those for the oxidizing electrodes, which have presented the major problems to date. Relatively high

-252-

conductivity phases have been found among cobaltates and chromates as reported by Tretyakov and Schmalzried (1965). $CoCr_2O_4$ doped with manganese was used in the Westinghouse development, as reported by Sverdrup et al. (1965) and by Sun et al. (1971). There is not much information available on the interconnector performance of itself. The Westinghouse cells operated for intervals up to about a thousand hours but with relatively low power density output; the cells yielded approximately 0.1 watts per cm^2, which is significantly less than the desired levels. The low output was not attributed to poor interconnector performance; thus, it can be concluded that such cells can be operated for an extended interval of time without breakdown of the interconnectors.

Another candidate material is (Sr,La) CrO_3 which has been developed as an electronic conductor for high temperature oxidizing environments, but has not as yet been incorporated into fuel cell development programs.

IV.   Comments on Performance and Cost Expectations Relating to High Temperature Solid Fuel Cells

A.   Introduction

It presently seems reasonable to expect that solid electrolyte fuel cells of the type discussed here can operate with current densities greater than 350 milliamperes per cm^2. This will result in power values of about 0.5 watts per cm^2 of active cell area. When such cells are assembled into reasonable configurations, this should produce a power density between 5 and

15 kilowatts per cubic foot (kw/ft^3) of cell assembly.

B.   Available Cost Estimates

Cost estimates by Sverdrup et al (1972) indicate a materials cost of about $20.00 per kilowatt at the present time, as well as a processing cost of $20.00 per kilowatt. They estimate that with larger scale production, the sum of these costs could be reduced to about $30.00 per kilowatt of fuel cell output for the fuel cell assembly itself. However, in addition there are other costs associated with the overall system and it is these other costs which have dominated the economics of this type of system to date.

According to Sverdrup et al. (1972), the Westinghouse system, which is designed to utilize coal as a fuel and therefore includes other components such as a coal reactor and gas cleaning and recirculation equipment, could be in the vicinity of $130.00 per kilowatt of generator rating.

According to Markin (1972), the costs of the system being developed at the Atomic Energy Research Establishment in England, which has been designed to use gaseous hydrocarbon as fuel, are dominated by the economics of the gas reforming equipment necessary to reduce the carbon activity in the fuel in order to prevent carbon deposition in the cooler parts of the system.

It is quite evident that the cost of the operational parts of this type of high temperature solid electrolyte fuel

-254-

cell is quite low. Thus its use in the electrochemical com-
bustion of hydrogen appears very attractive since the utilization
of hydrogen as a fuel avoids the necessity for the expensive
parts of the system involved in the present developmental programs
aimed at the utilization of carbonaceous fuels.

C. Comments on Ceramics Fabrication Costs

High quality thin walled tubing of standard ceramic
materials currently costs approximately $1.00/inch length for
1/2" diameter tubes. This gives a cost/area value of $0.20/cm^2.
With a demonstrated power output of 0.5 watts/cm^2 in experimental
cells, the base price projected for power plant use would be
$400.00/kw if one were to use this approach to cost estimation.
Other components to be added and operations to be conducted will
raise this estimate. These numbers conflict with the estimates
reported by Sverdrup et al (1972) mentioned earlier. Thus it
seems clear that a major reduction in fabricated ceramic costs
is critical. A reduction of a factor of 10 is needed for a sys-
tem with competitive capital cost. Although specific data were
not cited, Bueche (1973) commented that materials costs "were
found to constitute a barrier that an all-out scientific assault
failed to penetrate," and that this governed G.E.'s low ranking
of fuel cells for potential power conversion systems.

-255-

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$$\frac{1}{2} H_2 \longrightarrow H^+ + e^-$$ $$\frac{1}{2} O_2^2 + 2e^- \longrightarrow O^2$$
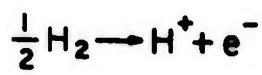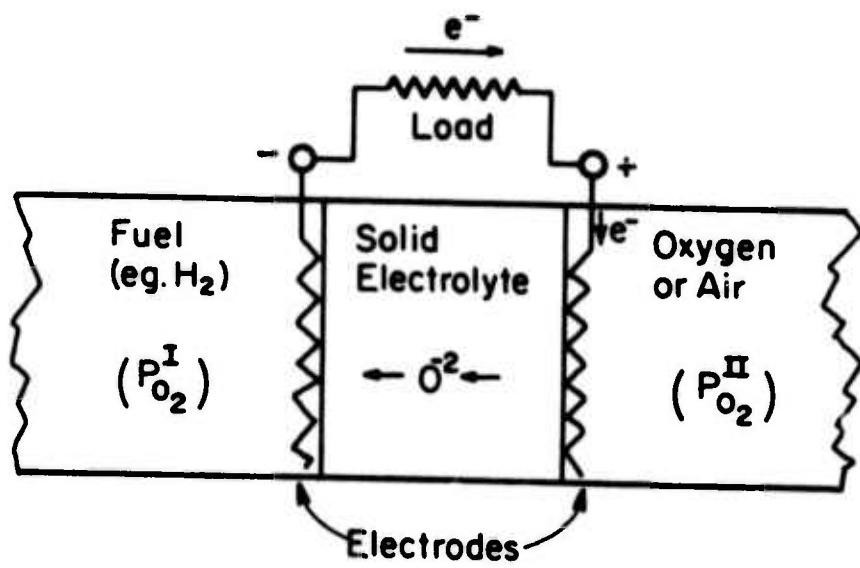
Figure 1.   Schematic Representation of Solid Electrolyte Fuel Cell.
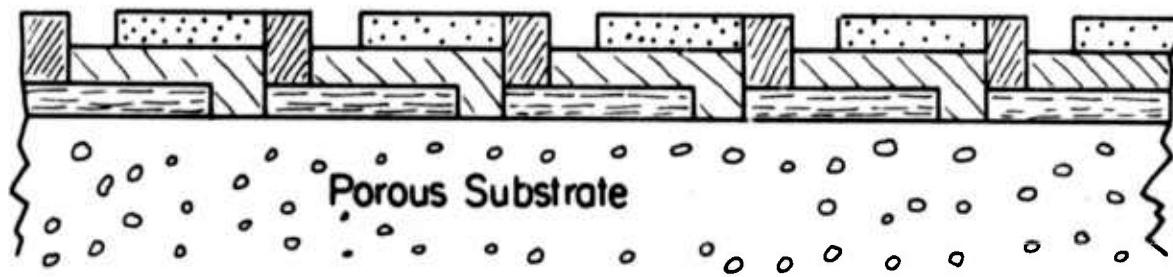
	Solid Electrolyte
	Interconnection
	Air (Oxygen) Electrode
	Fuel (H₂) Electrode

Figure 2.   Schematic Illustration of Multiple Layer Thin
Film Design of High Temperature Solid Electro-
lyte Fuel Cell.

COMMENTS ON THE USE OF A HIGH EFFICIENCY
SOLID ELECTROLYTE THERMOELECTRIC TRANSDUCER
SYSTEM AS A SOLAR ENERGY CONVERTER

W. H. Flygare
R. A. Huggins

Abstract

It is proposed that consideration be given to the use
of a thermoelectric device involving the use of a solid electro-
lyte and isothermal expansion of sodium for solar energy con-
version.

The theoretical principles involved in such a device
have been discussed, and the theoretical efficiency calculated.
It has been shown that the theoretical efficiency in such a
system is much higher than that of conventional thermoelectric
devices, closely approaching the Carnot limit.

Because of its inherent simplicity and low materials
cost, major practical limitations or disadvantages do not appear
likely.

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-261-

COMMENTS ON THE USE OF A HIGH EFFICIENCY
SOLID ELECTROLYTE THERMOELECTRIC TRANSDUCER
SYSTEM AS A SOLAR ENERGY CONVERTER

W. H. Flygare
R. A. Huggins

This report is an analysis and commentary relating to
the use of a solid electro-based thermoelectric generator
for the conversion of thermal energy to electrical energy. The
basic idea involves a simple electrochemical cell as illustrated
in Fig. 1. This basic design has been described in the patent
literature[1-3] but the analysis given here is based upon our
understanding of the principles involved.

On the high temperature (T_2) Na liquid side of the
β-alumina electrolyte an electron is given to the electrode.
The Na^+ ions diffuse through the β-alumina to the other electrode,
which supplies an electron, converting Na^+ back to Na. The Na,
still at temperature T_2, then evaporates and is condensed at a
lower temperature T_1. The liquid at T_1 is then pumped up to the
reservoir at pressure P_2. Heat is absorbed from the external
environment to bring the liquid Na from T_1 to T_2.

The emf generated in the $Na \rightarrow Na^+ + e^-$ and $Na^+ + e^- \rightarrow Na$
half reactions due to the pressure gradient across the β-alumina
solid electrolyte at T_2 is given by

$$E_p = \frac{RT_2}{nF} \ell n \left(\frac{P_2}{P_1} \right) \tag{1}$$

where T_2 is the local temperature at the electrolyte, and P_2 and P_1 are the equilibrium pressures at temperature T_2 and T_1, F is the Faraday constant and n is the number of electrons transfered per Na atom. The back emf E_b due to the Na^+ ion current flow through the combined β-alumina and electrode structure resistance R_o (ohm cm^2) is

$$E_b = iR_o \tag{2}$$

where i is the Na^+ ion current. Thus the total emf E, developed by the Na^+ ion transport is given by

$$E = E_p - E_b \tag{3}$$

or

$$E = \frac{RT_2}{nF} \ell n \left(\frac{P_2}{P_1} \right) iR_o \tag{4}$$

Since the power, P, is Ei,

$$P = i \left[\frac{RT_2}{nF} \ell n \left(\frac{P_2}{P_1} \right) \right] - i^2 R_o \tag{5}$$

the maximum power as a function if i is given by

$$\frac{dP}{di} = 0 = \left(\frac{RT_2}{nF} \right) \ell n \left(\frac{P_2}{P_1} \right) - 2iR_o \tag{6}$$

giving a current at maximum power, i_{max}, of

$$i_{max} = \frac{RT_2}{nF} \ell n \left(\frac{P_2}{P_1} \right) \tag{7}$$

and a maximum power of

$$P_{max} = \frac{1}{2R_O} \left[\frac{RT_2}{nF} \ell n \ \frac{P_2}{P_1} \right]^2 - \frac{1}{4R} \left[\frac{RT_2}{nF} \ell n \left(\frac{P_2}{P_1} \right) \right]^2$$

$$= \frac{1}{4R_O} \left[\frac{RT_2}{nF} \ell n \left(\frac{P_2}{P_1} \right) \right]^2$$

(8)

$R = 8.31$ joules/deg. mole

$F = 96,487$ coulomb/mole

$$P_{max} = \frac{1}{4R_O} \left[8.613 \times 10^{-5} \ T_2 \ \ell n \left(\frac{P_2}{P_1} \right) \right]^2$$

Figure 2 shows a plot of P_{max} as a function of T_2 for various values of T_1 and R_O, and using the vapor pressure data shown in Table I. The curves in Fig. 2 show the expected dependence on the values of the lower temperature, T_1. In actual practice the low temperature limit will probably be determined by a balance between heat flow out to the external heat sink radiation and conduction heat transfer in from the portion of the system at temperature T_2. A low temperature slightly above the melting point at $T \simeq 400°K$ seems quite feasible. However, because of the energy used in reheating the liquid Na from T_1 to T_2, the overall system efficiency may be optimized if T_1 is somewhat higher.

It is quite evident that it is advantageous to achieve as low a value of R_O as possible. A resitance R_O of 0.1 ohms cm^2 seems reasonable for a beta alumina electrolyte of a few millimeters thickness in series with a thin layer of Na-permeable electrode material.

As pointed out by Weber[3], the nature of the electrode material from which the evaporation occurs is an important practical consideration in such devices. According to Fig. 2, about 1 watt/cm^2 is achievable with T_2 near the Na boiling point if $R_0 \simeq 0.1$ ohm/cm^2 and $T_1 = 400°K$.

The efficiency of this thermoelectric transducer is the ratio of the work done divided by the heat absorbed in cycling the Na around the closed system described in Fig. 1.

$$\text{Efficiency} = \varepsilon = \frac{W_1 - W_2}{L + q_1 + q_2} \qquad (10)$$

where

W_1 = Work done in expanding the gas from P_2 to P_1 at T_2

W_2 = Work done in pumping the Na fluid against a pressure difference $P_2 - P_1$

L = Latent heat of vaporization of Na

q_1 = Heat absorbed during isothermal expansion of Na

q_2 = Heat content (enthalpy) difference in liquid Na between T_2 and T_1

When the Na vapor cools from temperature T_2 to T_1 heat is released which goes into the sink at T_1. Likewise, the heat given off upon recondensation of the vapor is also lost to the sink at T_1. However, neither of these enters the efficiency relation. We can now evaluate the quantities in Eq. (10) for a specific example; choose $T_1 = 400°K$ and $T_2 = 1100°K$. The

following results are found for one mole of Na.

$$W_1 = RT_2 \ln P_1/P_2 = 2.0(1100) \ln\left[\frac{5.69\times10^{-1}}{1.59\times10^{-5}}\right] = 43,128 \text{ cal/mole}$$

$$W_2 = (P_2-P_1) \; V_{\text{mole(Na)}}$$

However, W_2 is much smaller than W_1, so we can write

$$W_1-W_2 \simeq W_1$$

The remaining numbers needed in Eq. (10) are

$$L \quad 23,400 \text{ cal/mole}$$

$$q_1 = W_1 = 43,128 \text{ cal/mole}$$

$$q_2 = (7 \text{ cal/mole})(T_2-T_1) = 4900 \text{ cal/mole}$$

Thus,

$$\varepsilon = \text{Efficiency} \simeq \frac{43,128}{71,428} = 0.604$$

This can be compared to the Carnot efficiency of

$$\varepsilon_c = \frac{T_2-T_1}{T_2} = \frac{700}{1100} = 0.636$$

Thus, the theoretical efficiency of the proposed thermoelectric generator, assuming no heat losses and a 100% efficient pump, is very nearly equal to the Carnot efficiency, which is the maximum efficiency for a heat engine of any type.

More conventional approaches to thermoelectric generation devices, such as those based upon thermionic emission or the Seebeck effect, suffer two major disadvantages compared to this approach. They characteristically have a temperature

-266-

gradient across the conducting solid (or liquid) portion. As a result, there is a substantial amount of energy loss due to irreversible heat transfer down this temperature gradient.

In addition, these solid-state thermoelectric devices typically have much lower values of driving force (voltage) than is the case in this system. This is an important point, as electrical transmission losses are reduced by operation at higher voltage/current ratios.

As a result of these factors, the efficiency of conventional thermoelectric and thermionic devices is generally only a few percent, much lower than that of the system described here.

Although this type of a thermoelectric energy transducer is relatively recent, it is related to the several "thermally regenerative cells" proposed[5-7] somewhat earlier. However, such thermally regenerative cells typically involve a molten salt electrolyte in contact with a liquid metal solution at T_1, from which the mobile element is evaporated for recycling to T_2. Thus, instead of the temperature, and therefore the vapor pressure, the driving force is provided by the free energy of solution in those systems.

However, the efficiency of the typical thermally regenerative cells[8-9], although much better than that of Seebeck effect and thermionic devices, is inherently much lower than for the evaporative system described here because of the much

lower activity ratio, and hence voltage, achievable in such systems. In addition, both the solvent and solute have to go through the thermal cycle.

Because of the unusually high values of inherent efficiency of this method of thermoelectric energy conversion; a system such as described here appears to be an attractive candidate for use with several of the methods currently being considered for the capture and utilization of solar energy.

The design is basically quite simple, with no moving parts. The important materials involved are all quite inexpensive, and there is no reason to expect major difficulties with design or construction.

It has been reported[3] that electrical power outputs of 500 milliwatts per cm^2 of electrolyte surface appear to be feasible in practical systems, so that such devices need not be exceedingly large or cumbersome.

Acknowledgement

-268-

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TABLE I. <u>Sodium Vapor Pressure Data</u>[4]

	T(°K)	P(atm)
	298.15°	2.64×10^{-14}
	325.	9.66×10^{-13}
	350.	2.15×10^{-11}
MP	370.98	1.35×10^{-10}
	400.	1.59×10^{-9}
	500.	8.43×10^{-7}
	600.	5.19×10^{-5}
	700.	9.74×10^{-4}
	800.	8.60×10^{-3}
	900.	4.68×10^{-2}
	1000.	1.93×10^{-1}
	1100.	5.69×10^{-1}
BP	1156.2	1.00
	1200.	1.50
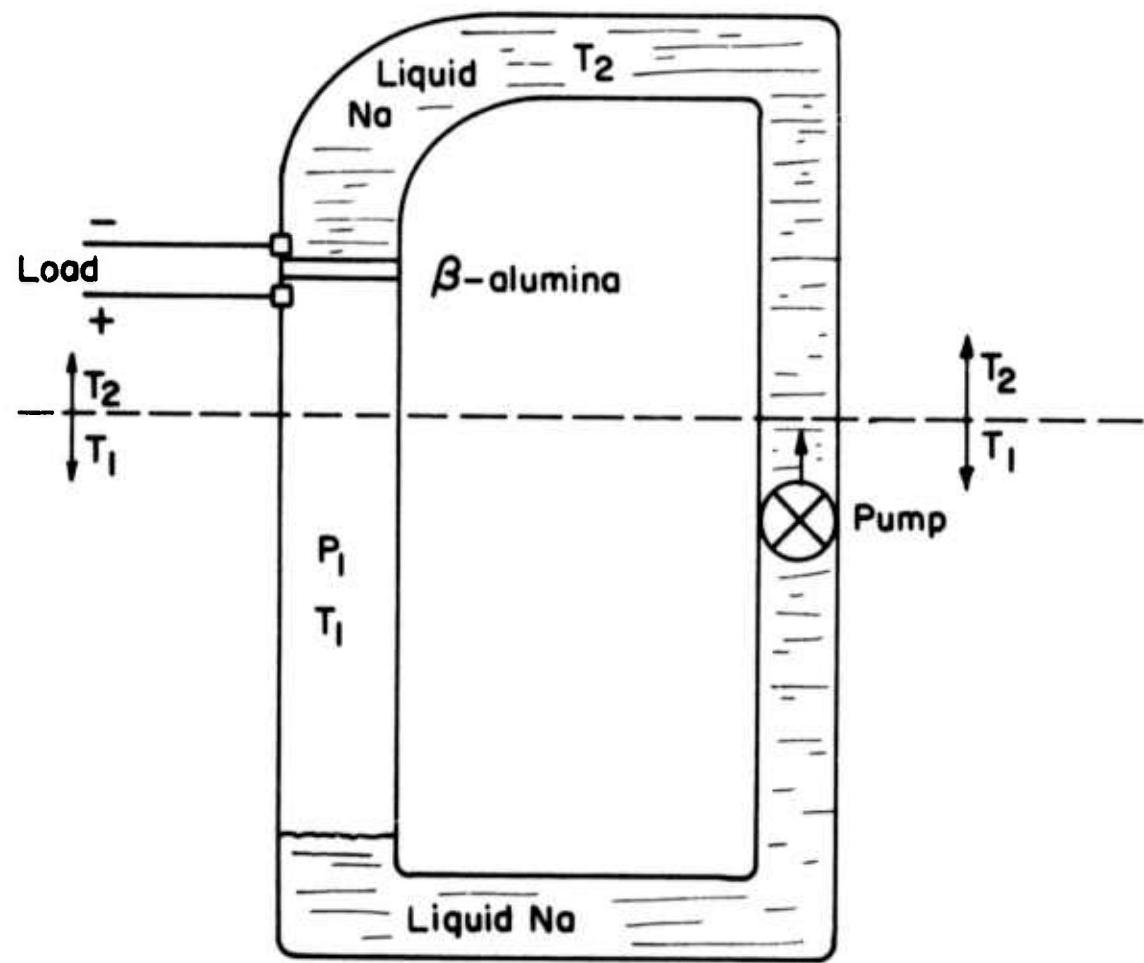
P_2 is vapor pressure of Na at T_2 (high T)

P_1 is vapor pressure of Na at T_1 (low T)

Figure 1.
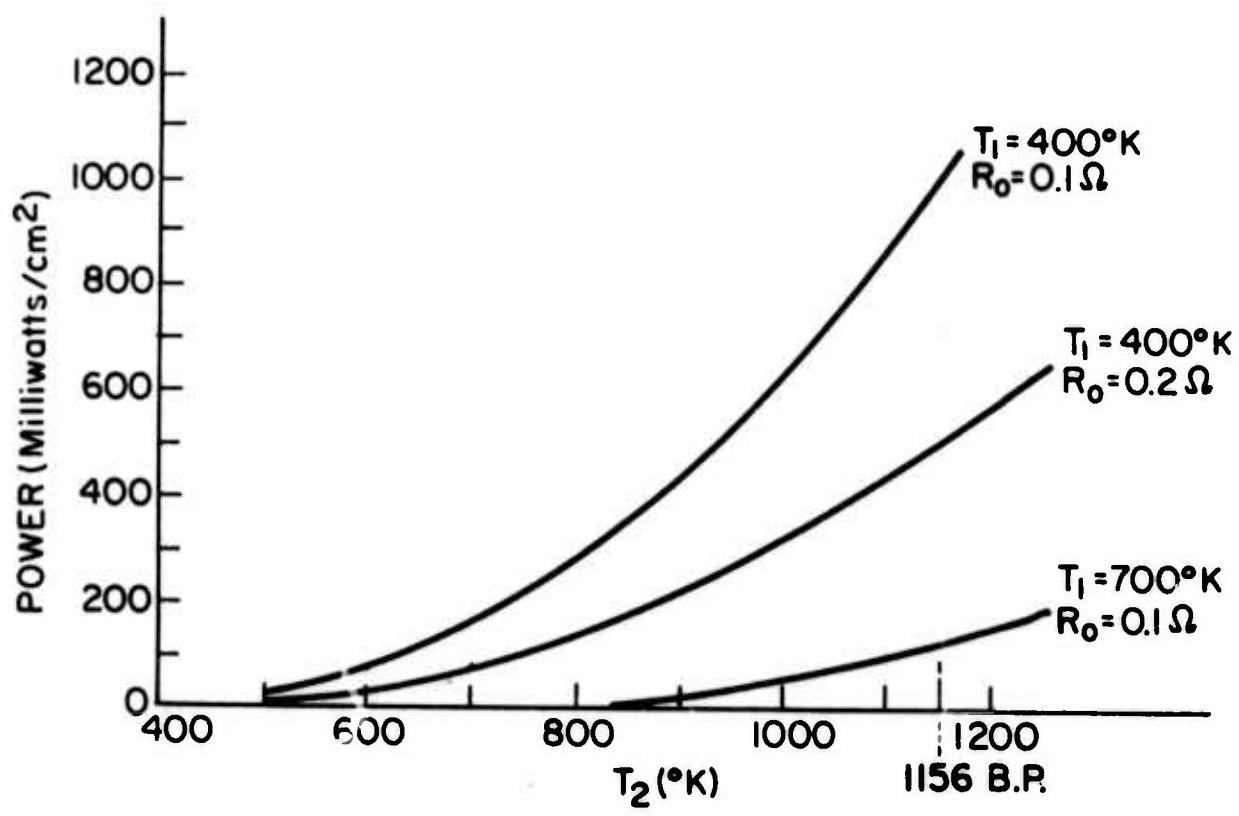
Figure 2.

Proposal for a

PROGRAM ON INTEGRATED SOLAR ENERGY SYSTEMS FOR MILITARY BASES

Proponent: DoD - ARPA

Category: Decentralized Conversion (Primary)

                  Energy Transmission, Distribution, and
                  Storage Technology (Secondary)

Sub-Programs: 1. Pilot-Plant Design, Construction, and
                      Testing

                  2. Materials Technology

                  3. Component Design and Testing

A five-year program is described, leading to construction of a 2 MW thermal/electrical solar energy pilot plant on a military base and directed towards construction of a 50 MW demonstration-level integrated solar power system. The five-year program calls for an expenditure of $25.5 million.

TABLE OF CONTENTS

274<

ENERGY RESEARCH AND DEVELOPMENT

Program Proposal: Fiscal Year 1975 Through Fiscal Year 1979

TECHNOLOGY EVALUATION

GENERAL DESCRIPTION OF THE PROGRAM

Proponent: DoD-ARPA

A. **PROGRAM**: Integrated Solar Energy Systems for Military Bases

Category: Decentralized Conversion (Primary)

Energy Transmission, Distribution, and Storage Technology (Secondary)

B. **SUB-PROGRAMS**: 1. Pilot-Plant Design, Construction, and Testing

2. Materials Technology

3. Component Design and Testing

C. **DESCRIPTION**: The purpose of this program is to develop integrated solar energy systems to supply multiple energy needs for military bases. The diverse energy requirements to be supplied include building heating and comfort conditioning; building auxiliary power supply, industrial heat and electrical supply; water heating, purification, and recycling; and battery-powered transportation. Optimal system integration among various types of solar conversion elements, auxiliary sources of energy supply, and energy transmission, distribution, storage, and control systems will be required to satisfy the specific energy requirements for military bases. These include long-term

independence, reliability, flexibility, and
security of supply; multipurpose energy
utilization; economy; applicability to remote
or unusual site conditions; and short con-
struction time and ease of achieving beneficial
use.

The proposed program emphasizes an early
exploitation of current technology as aug-
mented with advanced system modeling concepts,
solar conversion techniques, materials and
materials processing technology, and building
layout and thermal insulation methods to design,
construct, and test a 2 MW pilot plant (time-
averaged energy supply capacity) by the end
of Fiscal Year 1979. It is recommended that
this pilot plant be located at an existing
military base and, to the extent possible,
be integrated into the energy supply and
utilization plan for that base. Operation of
the pilot plant will be designed to evaluate
the following system characteristics:

(1) Overall system conversion efficiency,
    capacity, and reliability;

(2) Overall system energy balance and con-
    servation;

(3) Economics of capital investment, fuel
    supply, and system operation and
    maintenance;

(4) Environmental impact; and

(5) Potential changes to existing codes and specifications for building design and construction; for energy generation, transmission, and distribution; and for transportation systems.

Data generated during this phase of the program will be compared with quantitative estimates provided by analytical system models and will contribute to the design criteria for a demonstration plant of 50 MW time-averaged capacity (electrical plus thermal) by Fiscal Year 1983.

The realistic development of solar energy systems for terrestrial applications will require substantial efforts in materials technology as well as in component design and testing. These requirements are identified in separate sub-programs under the overall program; the sub-programs will involve a high degree of interagency coordination. It is also expected that the integrated solar energy system as defined in the program and the opportunity for an early technical demonstration of a pilot plant under DoD project management will provide valuable experience and information for civilian solar energy development.

SUB-PROGRAM 1

PILOT-PLANT DESIGN, CONSTRUCTION, AND TESTING

a. Comparison with Existing Technology

Solar energy utilization is characterized by a number of assets, in comparison to fossil-fueled space-conditioning and electrical power generation, and in comparison to other "exotic" technologies.

* The primary source of energy is ubiquitous and fairly evenly distributed.

* The foreseeable, adverse environmental effects are minimal.

* The total available sunlight is sufficient, in principle, to provide a major portion of the power requirements for the nation. A reduction of dependency on foreign fuel supplies would result from significant utilization of solar energy for space conditioning and electricity generation. The use of solar power to generate "artificial" fuels (not part of the present program) could potentially reduce dependence on foreign fuels still further. For the long term, solar energy may be the only realistic option if neither breeder reactors nor fusion reactors succeed.

* The relative efficiency of combined solar panels,using both photovoltaic and thermal collectors, and utilizing an appreciable portion of the power directly for space and water heating, is expected to be high; such systems are thought to be closest to achieving economic success among the various solar utilization possibilities.

A number of potential liabilities in the success of these solar technologies also exist:

* Such plants tend to be capital-intensive.

* Architectural restrictions accompany the use of structure-integral units.

* Significant land allotments are required for "detached" electricity-generating units.

b. Significant Technical Uncertainties

Several technical obstacles stand in the way of the completely economic implementation of full-scale, integrated solar systems.

It is one of the intents of the present program to bring such obstacles into sharp focus in a complete system and to assist in their solution. The hurdles listed below will not prevent construction of the proposed pilot plant, but if they are not overcome during the period of the program, the future viability of the corresponding portions of the system will be open to question.

* Sufficiently low production costs must be achieved for the photovoltaic elements, together with adequate efficiency and durability.

* For the "detached" system, sufficiently low construction costs must be achieved for solar concentrators and for the thermal collector/transfer conduits.

* Maintenance procedures of acceptable simplicity and cost must be demonstrated.

* The reliability of relatively complex, yet necessarily inexpensive, control systems must be demonstrated.

* The overall system must demonstrate a capacity to handle an adequate portion of the total power requirements reliably, without (through failure or lack of adequate storage) placing an undue load on auxiliary power supplies.

c. Constraints

There is relatively little geographic constraint relative to the system proposed, except as may be imposed through portions of the system which require land use beyond the area of the structures themselves. An important external constraint lies in the realm of building and engineering codes, which will probably not allow the most efficient implementation of structure-integral units initially.

d. Significant Capital Investments

The major thrust of this program, of course, is the construction of the pilot plant, which will represent a significant capital investment. It is assumed that the funds specifically allocated in this program for construction costs will be only incremental to the basic construction costs for new structures scheduled to be built within the applicable time interval.

e. Government/Private Sector

The proposed program is planned to be entirely Federally funded. However, a major portion of the funds will be expended through industrial contracts and industrial vendors. It is anticipated that the program, leading to the construction of a pilot plant, will provide considerable incentive for additional development activity by industry.

f. Supporting Rationale

While there have been valid reasons for the existence of isolated projects on materials research and development, component design, and system studies for solar energy utilization, it is now opportune to provide a real focus for such efforts in the construction of a pilot-plant which is to have actual beneficial output in a populated environment. The pilot-plant which is anticipated for this program will comprise (a) solar units which are integral components of buildings, for which they will provide both space conditioning (heating, cooling and humidity control) and electrical power, and (b) a detached unit, referred to as a Solar Power Module Loop, which could generate electricity and process heat, in possible combination with water purification.

Thus, the pilot plant will provide a test for many of the concepts which have already been developed as well as an opportunity to further develop requirements for an integrated system, including thermal and electrical storage, and distribution and control facilities. Within the framework of the present program the opportunity will also exist to study other concepts which may be of special interest within DoD, such as component portability, modularity, ease of assembly, and other factors which relate to temporary, portable, or remote facilities.

The proposed program, in addition, takes advantage of the unique role which DoD can play through its existing organizational and military-base structure, in terms of providing complete localization and monitoring of the functional requirement specifications, architectural designs, engineering, and construction of the pilot plant and subsequent demonstration plant.

The accompanying milestone chart summarizes the projected stages of design, construction, and testing for the pilot plant. This includes the modeling of various energy supply and load mixes, architectural design of buildings with instrumented heating and conditioning equipment, site selection and preparation, and construction of the integrated solar energy system. Provision is also made for the performance testing of the pilot plant for eventual scale-up to a full-size demonstration plant beyond the scope of the present program. The pilot plant experience will also help develop guidelines for potential changes in building codes and specifications, and will generate technical and economic data for the potential applicability of solar energy systems to civilian communities.

SUB-PROGRAM MILESTONE CHART: PILOT-PLANT DESIGN, CONSTRUCTION, AND TESTING

Fiscal Year →	75	76	77	78	79
1. System Design	△1		△2	△3	
2. System Construction		△4	△5	△6	
3. System Testing			△7	△8	△9

△1 Completion of system modeling and scoping design. Decision on pilot-plant capacity and load mix.

△2 Completion of preliminary design of energy conversion system and architectural layout of structures and auxiliary components. Completion of environmental impact statement.

△3 Completion of detailed design.

△4 Completion of test-site survey.

△5 Completion of test-site preparation.

△6 Completion of structures and integrated solar energy system. Delineation of beneficial uses.

△7 Completion of testing plan and procedures.

△8 Installation of test instrumentation and start of testing.

△9 Decision on verification of short-term test criteria. Recommended modifications to building codes and specifications.

Decision on program continuation through to full-scale demonstration plant.

282<

SUB-PROGRAM 2

MATERIALS TECHNOLOGY

a. Comparison with Existing Technology

> N/A

b. Significant Technical Uncertainties

Achievement of economical demonstration and full-scale plants of the type planned for the pilot plant will require the achievement of particular materials goals in the areas of surface optical properties and durability at operating temperatures, of the durability and fabrication costs of photovoltaic cells, and of the surface durability of windows and mirrors. Failure to achieve adequate properties in any of these areas during the time period of the present program may face subsequent design changes and/or retrenchment regarding the portion of total energy requirements to be derived from solar energy.

c. Constraints

> N/A

d. Significant Capital Investments

> N/A

e. Government/Private Sector

> (See Sub-Program 1.)

f. Supporting Rationale

Solar energy utilization is particularly and uniquely dependent on specific materials properties and costs to a degree which demands that a strong thrust of the program be directed towards materials technology. Solar collection and conversion is dependent on low-cost processing and fabrication techniques, because of the low

energy density of sunlight; at the same time, practical efficiencies are sensitive to certain materials properties (such as surface optical behavior and photo/electronic behavior) which press on the frontiers of materials research and characterization. This circumstance is recognized in the present program through establishing Materials Technology itself as a separate sub-program. This sub-program will provide support to the overall program in terms of:

Materials selection,

Materials criteria specification,

Development and specification of materials characterization and testing procedures,

Compilation of data from existing technology,

Support of new materials development,

Support of process development,

Design and construction of pilot-scale process demonstrations, and

Support of advanced materials research.

During July 1973 the ARPA Materials Research Council listed certain directions for materials development thought to be of high potential for solar energy utilization. These will provide some initial guidance for the developmental and research aspects of the present sub-program. A number of the salient points identified by the Council are extracted below:

1. Concentration and Collection of Sunlight for Thermal Systems

    1.1 A three-pronged search for surfaces with special optical properties for radiative insulation should be pursued. Each of the three aspects may be realized in the near future; indeed, adequate materials may already exist.

        1.1.1 A surface material that is stable for long periods ($\sim$20 years) at high temperatures ($\sim$550° C) is needed for high light-concentration systems; for this purpose, sunlight-absorption/infrared emission

(α/ϵ) as low as 2 may be acceptable.

1.1.2 A heat-mirror surface with high transparency for sunlight and high reflectivity for infrared will prove useful for supplementing or replacing low ϵ coatings in the absorbing surface.

1.1.3 A surface material with very high α/ϵ for use in low-temperature systems ($\sim$250° C) without light concentration should be sought; the low operating temperature will lessen the problem of thermal degradation. A new concept based on the use of small metal particles ($\sim$100 Å) should be explored.

2. Photovoltaic Cells

2.1 New emphasis should be placed on terrestrial operations without the special requirements of outerspace applications, the latter having hitherto dominated the field. Emphasis should be placed on low cost and durability; standards of reliability can be lowered.

2.2 The physics and metallurgy of heterojunctions need to be better understood, especially the degradation processes in otherwise economical materials, such as Cu-Cd-S.

2.3 Improved techniques for characterizing surfaces and interfaces during the fabrication of cells are necessary.

2.4 The role of grain boundaries in photovoltaic cells requires elucidation, inasmuch as polycrystalline materials are much less expensive than the currently used single crystals.

2.5 The possibility of developing low-cost fabrication techniques for stacked photocells, with graded energy gaps which will effectively utilize a greater portion of the sunlight wavelength distribution should be examined.

2.6 Materials for photovoltaics should be considered in terms of their own requirements since these may be different than for semiconductors used in other electronic devices.

3. Special attention must be directed to energy-storage systems, which are a common requirement for virtually all means of solar energy conversion. The development of improved thermal-insulation materials for both high and low temperatures would also be beneficial.

SUB-PROGRAM MILESTONE CHART: MATERIALS TECHNOLOGY

Fiscal Year →	75	76	77	78	79
1. Materials Selection and Design Support	△1	△3	△5 △6	△7	
2. Materials Development		△2	△6		
a. Selective Absorbers and Reflectors			△5		
b. Mirror Surfaces			△5		
c. Photovoltaic Materials		△4			
d. Thermal Insulation					
e. Energy Storage Materials					
3. Process Technology		△4	△5 △6		
4. Advanced Technology					

△1 Critical materials selected for initial test components. Data compilations prepared from existing technology.

△2 Establish field-testing program for determining the long-term durability and reliability of candidate solar materials for the pilot plant.

△3 Materials-design criteria and performance specifications completed for preliminary pilot-plant design.

△4 Decision to select a near-term candidate photovoltaic material for pilot-scale process demonstration of fabrication costs.

△5 Decision on optimization of design of solar collector based upon the combined performance of selective absorber, infrared reflector, and solar mirror surface. Define product and process specifications and project fabrication costs.

△6 Decision on selection of primary and backup materials for pilot-plant design based on materials testing program and process development; also identify advanced candidate materials that warrant further testing.

△7 Completion of final materials specifications for major component procurement.

SUB-PROGRAM 3

COMPONENT DESIGN AND TESTING

a. Comparison with Existing Technology

Since the components of a solar energy utilization system are entirely different from those with which the existing energy conversion industry normally deals, adequate design and testing facilities do not now exist. This sub-program is intended to fill that need.

b. Significant Technical Uncertainties or Obstacles

N/A

c. Constraints

N/A

d. Significant Capital Investments

Approximately 25% of the total expenditure under this sub-program is expected to be devoted to capital equipment toward establishing a significant unique test facility for components of solar systems.

e. Government/Private Sector

(See Sub-Program 1.)

f. Supporting Rationale

A major aspect of this sub-program is to construct a testing facility for the components of solar energy conversion systems, especially in those fields where industrial testing facilities are not yet well developed. The facility is to be designed to handle a variety of component designs and mixes. Test apparatus and personnel will have capability in both direct (photovoltaic) conversion and thermal collection and conversion technology, as well as in both high sunlight

concentration and low (or no) concentration designs. The
facility will also have capability for testing combined units
(e.g., non-concentrating panels) comprising both photovoltaic
and thermal collection subcomponents. Test facilities for
control systems will also be established, particularly in
relation to the distribution of energy among the collectors,
electrical generators, and other sources, storage media and
loads comprising an integrated system. As noted in the cost
tables, this facility will represent a substantial capital
investment; it is anticipated that the investment will provide
continuing beneficial use, going beyond its role as a test
facility for the components of the pilot plant in the
immediate program.

A second major aspect of the sub-program will be to
establish the design for the construction of system components
for the immediate pilot-plant program. In that process, the
technical and economic aspects of various mixes of concentra-
tion and conversion schemes will be examined (as applicable),
as well as durability and reliability parameters. In connection
with this aspect of the sub-program, the project will play an
important role in determining configuration standards, unit
sizes, ratings, and so forth. A major beneficial output of
this sub-program will be to provide an initial framework for
industrial standardization of the component parts of solar
systems.

The milestones for the sub-program are considered in terms
of five topics. The first of these, Solar Conversion Panel,
relates to units designed to be an integral component of

structure and intended to provide the primary energy source for space conditioning as well as electrical power. As presently conceived, such panels would include both photo-voltaic and thermal collectors, the latter furnishing the major input for space conditioning and the former direct electrical power. Existing considerations indicate that substantial efficiency advantages accrue through such a "tandem" system; one of the major technical decisions to be made through this sub-program, therefore, is to determine whether such combined panels are technically and economically feasible, and the relative merits of various combinations of materials and configurations.

The second topic, Solar Collector Module Loop, relates to components for a "detached" electrical generating capability, not constructed as an integral portion of the structures, but integrated into the common storage and distribution network. A variety of important technical decisions need to be made in this area, such as the optimal degree of solar concentration, mirror configuration, surface coating materials, etc. However, the most important decision to be made in this connec-tion is whether such a "detached" solar system - generating electricity - is both technically viable and affordable, within the pilot plant time and cost framework. Another major consideration of this portion of the design and test sub-program will be the extent to which this aspect can be efficiently combined with the fourth topic, Water Purification.

The third topic, Energy Storage and Distribution, requires a new and sophisticated facility for design and testing. Few

situations currently exist in which comparable control
facilities are available for thermal and electrical flow among
external and internal sources, storage media and loads. It
is anticipated that a major beneficial output from this portion
of the sub-program will be solid-state control circuit design
applicable to single-unit construction with solar energy input
and built-in thermal and electrical storage.

It is apparent that the field of component design for solar
collection is one in which inventiveness may be very fruitful,
both in achieving lower costs of fabrication and a higher
percentage utilization of the total sunlight. Establishing
this program will in itself provide incentive for
commercialization and related industrial developments. In
addition, the Component Design and Testing sub-program will
pursue a conscious effort to stimulate such work, especially
on the basis of measured shortcomings in initial designs.
This activity is indicated in the accompanying Milestone Chart
under the heading of Advanced Components.

230<

SUB-PROGRAM MILESTONE CHART: <u>COMPONENT DESIGN AND TESTING</u>

Fiscal Year →	75	76	77	78	79
1. Solar Conversion Panel	①①	②②	③③		
2. Solar Collector Module Loop	①①	②②	③③		
3. Energy Supply, Storage, and Distribution					
a. Solar Panel Test Facility	①①	②②	③③		
b. Solar Collector Module Loop Facility	①①	②②	③③		
4. Water Purification Component		①①	②②	③③	
5. Advanced Components					

△① Design and performance criteria established.

△② Design and construction of test units completed.

△③ Preliminary testing completed. ⌐Decision¬ on verification of system design criteria. Plans for continuation of testing reviewed.

PROGRAM Integrated Solar Energy Systems for Military Bases

SUBPROGRAM   **PROPONENT** DoD-ARPA

MILESTONE	DATE	BENEFICIAL OUTPUT		EFFLUENT OR WASTE	
		QUANTITY/RATE	UNIT(S)	TYPE(S)	QUANTITY/RATE(S)
THEORY ESTABLISHED	Exist-ing		(THEORETICAL LIMITS)		
ECONOMIC VIABILITY FORECASTED	Jan. 1975				
Component EXPERIMENT DESIGNED	Jan. 1975		~~(INVESTIGATIVE LIMITS)~~		
Initial COMPONENT TESTING Completed	May 1977	$1-2/ft^2 solar collector panel $2-4/ft^2 P/V panel	(INVESTIGATIVE LIMITS)		
BENCH MODEL COMPLETED	May 1977				
LABORATORY EXPERIMENTATION COMPLETED	June 1977	$2-3/MBTU solar heat 8-12¢/ton-hr solar cooling			
ENGINEERING DEVELOPMENT	Jan. 1978				
PILOT PLANT	June 1979	2MW Time-averaged (0.5 MW elec.)	70% plant availability	Thermal Discharge	(Not significant
DEMONSTRATION PLANT	1983	50 MW Time-averaged (30 MW elec.)	90% plant availability $1000/KW(e)	Thermal Discharge	(to be determined)
FIRST COMMERCIAL APPLICATION	1985				
SUBSEQUENT APPLICATION	1985				
	1991				

292<

COSTS

PROGRAM
SUBPROGRAM

Integrated Solar Energy Systems for
Military Bases

PROPONENT: DoD-ARPA

(in 10^6)

MILESTONE	THRU FY 74	FY 1975			FY 1976			AV: FY ___ THRU FY ___			TOTAL FY 75 THRU 79
		INVEST	OPER	TOTAL	INVEST	OPER	TOTAL	INVEST	OPER	TOTAL	
THEORY ESTABLISHED											
ECONOMIC VIABILITY FORECASTED											
EXPERIMENT DESIGNED											
COMPONENT TESTING (Sub-Program 3)	0	0.5	0.5	1.0	0.75	0.75	1.5	0.36	1.47	5.48	7.98
BENCH MODEL COMPLETED											
LABORATORY EXPERIMENTATION COMPLETED											
Materials ENGINEERING DEVELOPMENT (Sub-program 2)	0	0.4	1.1	1.5	0.35	1.4	1.75	0.3	1.2	4.5	7.75
PILOT PLANT * (Sub-Program 1)	0	0	0.5	0.5	0	0.7	0.7	2.0	0.85	3.55	9.75
DEMONSTRATION PLANT											
FIRST COMMERCIAL APPLICATION											
SUBSEQUENT APPLICATION											
Program Total	0	0.9	2.1	3.0	1.1	2.85	3.95	2.96	3.52	18.53	25.48

* Costs do not include buildings.

PROGRAM: Integrated Solar Energy Systems
SUB PROGRAM: for Military Bases

PROPONENT: DoD-ARPA

MILESTONES	PERSONNEL*			LAND AREA	WATER	FUELS		OTHER	
	SCI.	TECH.	ADM.			TYPE	QUAN.	TYPE	QUAN
THEORY ESTABLISHED									
ECONOMIC VIABILITY FORECASTED									
EXPERIMENT DESIGNED									
COMPONENT TESTING + (Sub-program 3)	0	63	63	minor	minor				
BENCH MODEL COMPLETED									
LABORATORY EXPERIMENTATION COMPLETED									
Materials ++ ENGINEERING DEVELOPMENT (Sub-program 2)	50	64	114	minor	minor				
PILOT PLANT +++ (Sub-program 1)	0	107	107	<50 acres	minor	prepare natural gas	20,000 gal/yr 20 KCMF/yr		
DEMONSTRATION PLANT									
FIRST COMMERCIAL APPLICATION									
SUBSEQUENT APPLICATION									

ENVIRONMENTAL IMPACT STATEMENT REQUIRED? Yes

FOR WHAT YEARS? Fiscal Year 75 - Fiscal Year 76

* Manyears over period FY75-FY79
+ @ $90K/my
++ @ $60K/my
+++ @ $35K/my

294<

COSTS AND OTHER RESOURCE REQUIREMENTS

ACCORDING TO NSF CATEGORIES

* Heating and Cooling of Buildings (including water purification)
* Photovoltaics
* Solar/Thermal

295<

Integrated Solar Energy for
PROGRAM: Military Bases
SUBPROGRAM: Heating and Cooling of Buildings*

PROPONENT: DoD-ARPA

(in 10^6)

MILESTONE	THRU FY 74	FY 1975			FY 1976			AV: FY ___ THRU FY ___			TOTAL. FY 75 THRU 79
		INVEST	OPER.	TOTAL.	INVEST	OPER.	TOTAL	INVEST	OPER	TOTAL	
THEORY ESTABLISHED											
ECONOMIC VIABILITY FORECASTED											
EXPERIMENT DESIGNED											
COMPONENT TESTING (Sub-program 3)	0	0.2	0.2	0.4	0.3	0.3	0.6	0.14	0.6	2.22	3.22
BENCH MODEL COMPLETED											
LABORATORY EXPERIMENTATION COMPLETED											
Materials ENGINEERING DEVELOPMENT (Sub-program 2)	0	0.1	0.3	0.4	0.09	0.35	0.44	0.07	0.3	1.11	1.95
PILOT PLANT (Sub-program 1)	0	0	0.25	0.25	0	0.35	0.35	1.0	2.42	4.26	4.86
DEMONSTRATION PLANT											
FIRST COMMERCIAL APPLICATION											
SUBSEQUENT APPLICATION											
Total	0	0.3	0.75	1.05	0.39	1.0	1.39	1.21	1.32	7.59	10.03

* Includes water purification

Integrated Solar Energy Systems
for Military Bases

PROGRAM:
SUB PROGRAM: Heating and Cooling of Buildings °

PROPONENT: DoD-ARPA

MILESTONES	PERSONNEL *			LAND AREA	WATER	FUELS		OTHER	
	SCI.	TECH.	ADM.			TYPE	QUAN.	TYPE	QUAN.
THEORY ESTABLISHED									
ECONOMIC VIABILITY FORECASTED									
EXPERIMENT DESIGNED									
COMPONENT + TESTING (Sub-program 3)	0	25	25	minor	minor				
BENCH MODEL COMPLETED									
LABORATORY EXPERIMENTATION COMPLETED									
Materials ++ ENGINEERING DEVELOPMENT (Sub-program 2)	12	16	28	minor	minor				
PILOT PLANT +++ (Sub-program 1)	0	54	54	minor	minor	propane natural gas	20,000 gal/yr 20 KCMF/yr		
DEMONSTRATION PLANT									
FIRST COMMERCIAL APPLICATION									
SUBSEQUENT APPLICATION									

ENVIRONMENTAL IMPACT STATEMENT REQUIRED? Yes

FOR WHAT YEARS? Fiscal Year 1975; Fiscal Year 1976

* Manyears over period FY75-FY79
+ @ $90K/my
++ @ $60K/my
+++ @ $35K/my
° Includes water purification

297<

PROGRAM: Integrated Solar Energy Systems for Military Bases

SUBPROGRAM Photovoltaics

PROPONENT: DoD-ARPA

(in $ 10^6)

MILESTONE	THRU FY 74	FY 1975			FY 1976			AV: FY ___ THRU FY ___			TOTAL FY 75 THRU 79
		INVEST	OPER.	TOTAL.	INVEST	OPER.	TOTAL	INVEST	OPER	TOTAL	
THEORY ESTABLISHED											
ECONOMIC VIABILITY FORECASTED											
EXPERIMENT DESIGNED											
COMPONENT TESTING (Sub-program 3)	0	0.15	0.15	0.30	0.23	0.23	0.46	0.11	0.43	1 62	2.37
BENCH MODEL COMPLETED											
LABORATORY EXPERIMENTATION COMPLETED											
Materials ENGINEERING DEVELOPMENT (Sub-program 2)	0	0.16	2.44	0.60	2.14	2.56	0.7	0.12	0.48	1.80	3.10
FILOT PLANT (Sub-program 1)	0.	0	0.12	0.12	0	0.18	0.18	0.5	0.21	2.13	2.43
DEMONSTRATION PLANT											
FIRST COMMERCIAL APPLICATION											
SUBSEQUENT APPLICATION											
Total	0	0.31	0.71	0.92	0.37	0.97	1.34	0.73	1.12	5.55	7.90

(in $ 10^6)

PROGRAM: Integrated Solar Energy Systems for Military Bases

SUB PROGRAM: Photovoltaics

PROPONENT: DoD-ARPA

MILESTONES	PERSONNEL			LAND AREA	WATER	FUELS		OTHER	
	SCI.	TECH.	ADM.			TYPE	QUAN.	TYPE	QUAN
THEORY ESTABLISHED									
ECONOMIC VIABILITY FORECASTED									
EXPERIMENT DESIGNED									
COMPONENT TESTING + (Sub-program 3)	0	19	19	minor	minor				
BENCH MODEL COMPLETED									
LABORATORY EXPERIMENTATION COMPLETED									
Materials ++ ENGINEERING DEVELOPMENT (Sub-program 2)	20	26	46	minor	minor				
PILOT PLANT +++ (Sub-program 3)	0	27	27	minor	minor	minor			
DEMONSTRATION PLANT									
FIRST COMMERCIAL APPLICATION									
SUBSEQUENT APPLICATION									

ENVIRONMENTAL IMPACT STATEMENT REQUIRED? No

FOR WHAT YEARS?

* Manyears over period FY75-FY79
+ @$90K/my
++ @$60K/my
+++ @$35K/my

299<

PROGRAM: Solar/Thermal
SUBPROGRAM:
PROPONENT: DoD-ARPA

MILESTONE	THRU FY 74	FY 1975			FY 1976			AV: FY___ THRU FY___			TOTAL FY 75 THRU FY
		INVEST	OPER.	TOTAL.	INVEST	OPER.	TOTAL	INVEST	OPER	TOTAL	
THEORY ESTABLISHED											
ECONOMIC VIABILITY FORECASTED											
EXPERIMENT DESIGNED											
COMPONENT TESTING (Sub-program 3)	0	0.15	0.15	0.30	0.22	0.22	0.44	0.11	0.44	1.65	2.39
BENCH MODEL COMPLETED											
LABORATORY EXPERIMENTATION COMPLETED											
Materials ENGINEERING DEVELOPMENT (Sub-program 2)	0	0.14	0.38	0.52	0.12	0.49	0.61	0.1	0.42	1.56	2.70
PILOT PLANT (Sub-program 3)	0	0	0.12	0.12	0	0.18	0.18	0.50	0.21	2.14	2.46
DEMONSTRATION PLANT											
FIRST COMMERCIAL APPLICATION											
SUBSEQUENT APPLICATION											
Total	0	0.29	0.65	0.94	0.34	0.19	1.23	0.71	1.07	5.34	7.55

(in 10^6)

Integrated Solar Energy
PROGRAM: Systems for Military Bases
SUB PROGRAM: Solar/Thermal   PROPONENT:
DoD-ARPA

MILESTONES	PERSONNEL *			LAND AREA	WATER	FUELS		OTHER	
	SCI.	TECH.	ADM.			TYPE	QUAN.	TYPE	QUAN.
THEORY ESTABLISHED									
ECONOMIC VIABILITY FORECASTED									
EXPERIMENT DESIGNED									
COMPONENT + TESTING (Sub-program 3)	0	19	19	minor	minor				
BENCH MODEL COMPLETED									
LABORATORY EXPERIMENTATION COMPLETED									
Materials ++ ENGINEERING DEVELOPMENT (Sub-program 2)	17	22	39	minor	minor				
PILOT PLANT +++ (Sub-program 1)	0	27	27	<50 acres	minor	minor			
DEMONSTRATION PLANT									
FIRST COMMERCIAL APPLICATION									
SUBSEQUENT APPLICATION									

ENVIRONMENTAL IMPACT STATEMENT REQUIRED?   Yes

FOR WHAT YEARS? Fiscal Year 75; Fiscal Year 76

* Manyears over period FY75 - FY79
+ @ $90K/my
++ @ $60K/my
+++ @ $35K/my